AMERICAN
DYESTUFF REPORTER

DEVOTED TO THE INTERESTS OF TEXTILE CHEMISTRY
• BLEACHING • DYEING • FINISHING • PRINTING •
AND THE NECESSARY MECHANICAL EQUIPMENT

"Circulated Everywhere Textiles Are Processed"

VOLUME 25 | MAY 18, 1936 | NUMBER 10

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Official Publication of the American Association of Textile Chemists and Colorists

THE OBJECTS OF THIS ASSOCIATION ARE:

"To promote increase of knowledge of the application of dyes and chemicals in the Textile Industry.

"To encourage in any practicable ways research work on chemical processes and materials of importance to the Textile Industry.

"To establish for the members channels by which the interchange of professional knowledge among them may be increased."

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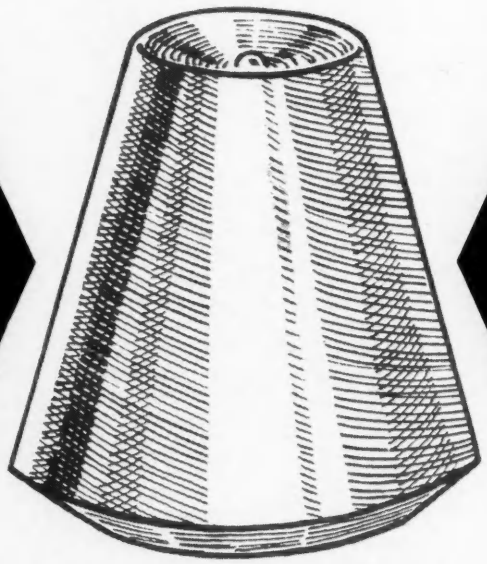

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AMERICAN
DYESTUFF REPORTER

VOLUME 25 MAY 18, 1936 NUMBER 10

What We've Learned From Interviewing

Members of Trade Associations

(Contributed)

IN ten years writing for business papers we have interviewed many members of trade associations. What has impressed us most is the different attitudes and reactions displayed toward association work by individuals united for cooperative effort toward a common goal. Although the fields covered vary from plumbing and heating to bakery products to automotive merchandise, we find that members of all trade associations fall into six general classifications. These classifications may not fit your particular association but here they are for your edification or diversion.

1:—The Wheel Horse. An association member who appreciates the value of teamwork and realizes that cooperative effort gets the load to the top of the hill. The Wheel Horse is always in harness working for association betterment, never needs the whip. At convention time he does more than sing, "The old gray mare". He knows that pulling alone gets him no where but brains and money pooling together is horse sense. Often he makes sacrifices to the detriment of his own business and health, unselfishly tugging at the traces for the common good. Unhitch the wheel horses and into the rut goes the trade association.

2:—The flea. Jumps on the membership rolls one year, jumps off the next. Usually "joins up" after the association has pulled a master-stroke of some kind or sometimes sensing a threatening development, he jumps to association shelter until the storm passes, then discontinues membership again. If he's lucky to survive, he does his flea act whenever propitious and so on ad infinitum. The flea never discontinues his fire or life insurance but business insurance—that can do a fade-out anytime. From our contacts with the flea we find that usually the real reason for his resignation is his desire to save money but his methods indicate to anyone experienced in business practices that he's blind as a bat.

3:—The pouter pigeon. Remember the spoiled child who picked up his marbles and went home when the game didn't suit him? He has grown up, gone into business and joined a trade association. But his mind works the same as in his marble days. He's still a spoiled child. Toward all cooperative efforts on the part of his broader-minded fellow members he displays petulance, criticizes, is defiant or apathetic. He shows his "independence" by refusing to attend meetings, withholding support when support is needed most but quickly criticizes the busy bees working continuously to right wrongs and to bring more milk and honey to all. The pouter pigeon forgets the constructive association work which benefits him every day but regarding fancied slights or minor errors, even in the distant past, his memory is elephantine. Although he cashes in on the benefits of his association, he always complains, "We would have made greater strides if things had been handled by more competent men". Often the pouter pigeon becomes a flea, then his excuse for jumping off the association band-wagon is, "I didn't like the fellows running it", "I find I can get along as well without it", "It never did me much good anyhow".

4:—The sloth. Receives favors but renders none. Joins an association only for what he thinks he can get out of it, not realizing that you get out of an association about what you put in it—with interest. Direct benefits, such as savings effected or losses avoided in specific instances are easy to credit to the source but it is hard to compute indirect association benefits, which are most important. Many association members have told us that affiliations made through contacts with other members and their friends have helped them solve many problems and increased profits. Through association bulletins and services, in meetings and at conventions, members capture that rara avis of business—new ideas and fresh viewpoints without which every executive is ready for the taxidermist.

5:—The nightingale. Belongs to an association mostly to get a chance to warble "Sweet Adeline" with the usual accompaniments at conventions and local shindigs. Seldom asks for or digests advice on modern business methods or operating procedure given by his association or trade papers. From observation, we can say that the nightingale's organization usually looks as old as "Sweet Adeline". Likewise, his methods. But, being a good mixer, the nightingale sometimes keeps out of failure's

trap without taking advantage of the many helps offered by his association and trade papers. He'd do much better if his business equipment and methods played a modern tune.

6:—The Chameleon. Attends meetings more to find out what others are doing than to offer cooperative services. Swears undying cooperation "for the good of our business", whenever the local boys get together to discuss their problems, but forgets all about it the next day and does as he pleases. The Chameleon is the first to slash prices indiscriminately, disrupt competition with profitless estimates and to do other things that undermine cooperation and destroy faith in the attainment of objectives without which no association can succeed.

Now, a word about the ostrich. This bird is always howling about the difficulty experienced in solving some problem, which the association in his field or the trade papers have already solved, yet, he never "joins up" and seldom reads his trade papers even if he subscribes, but continues to hide his head in the sand under the false assumption that the big, bad wolf of business inefficiency won't dig in after him. Our investigation has shown that the ostrich usually can afford it and is eligible to membership in a responsible association, his record is clean, yet, he never tries to get out of the jungle of bad management via that dependable combination—trade association and trade papers. Why? That's something we've never been able to figure out.

—— ◆◆ ——

Notes on

Cotton-Warp Sizing

By RALPH HART*

(Concluded from May 4th issue)

ELASTICITY AND STRENGTH OF YARN

Elasticity.—Because of the nature of starch, it will reduce the elasticity of the yarn; nevertheless the mill should endeavor to retain as much elasticity as possible in the sized warp. A yarn with a reasonable amount of stretch will give much better results on the looms than one with practically no elasticity and greater strength. A good sizing starch should reduce the elasticity of a yarn not more than 20 or 25 per cent. It is reported that cotton yarns between 20s and 30s have an elasticity from 4.5 to 5 per cent. As the count of the yarn increases, the elasticity diminishes; thus, yarns between 60s and 80s have an elasticity of 3.5 to 3.8 per cent, whereas those above 120s, from 2 to 3 per cent.

Breaking Strength.—In tests made with different proportions of starch, the breaking strength of two lots of sized yarn was found to be 31 per cent and 34 per cent, respectively, greater than that of the unsized yarn. The increase in breaking strength of 31 per cent was obtained on 22s yarn, sized with 280 pounds of thin-boiling starch, 14 pounds of softener and made up to 365 gallons. The test that showed an increase of 34 per cent was on 30s yarn, sized with 300 pounds of the same starch, 20 pounds of softener and made up to the same volume.

Effect of Humidity.—The greatest strength of sized yarn is reached at about 70 to 80 per cent relative humidity. Above that, it falls off about 10 per cent up to the state of wetness, on account of loss of strength of the softened starch. Sizing decreases the extensibility under dry conditions but the extensibility is rapidly regained with increasing humidity. At saturation it approximately equals that of the unsized yarn.

SIZING FORMULAS AND SIZE TAKE-UP

Formulas.—A number of mills reported that their size formulas contain the following percentages of starch, softeners, and gums:

Mill	*Starch* %	*Softeners* %	*Gums* %
A	90.9	7.6	1.5
B	92.8	6.5	1.7
C	88.7	11.3	...
D	92.0	8.0	...

The above percentages refer to solid ingredients only. On heavy and difficult weaves, such as 128 sley and 130 pick, at least 1 pound of starch was recommended to 1 gallon of finished size.

Amount of Size.—The English Cotton Research Institute makes the following statements: "Many difficulties in the weaving mills are due to the use of too much size. Too little size is only rarely responsible for disturbances in the weaving plants". It is stated that yarn is adequately sized when it has sufficient size on it to protect the surface against the raising of entangling hairs before the thread is formed into cloth. One mill reports that it adds 12½ per cent size, on 30s yarn, 1980 ends; another adds 9½ per cent size, on 8-ounce ticking.

Goods for Rubberizing.—Tentative specifications for cotton goods for rubber and pyroxylin coating as published by Committee D-13 of the American Society of Testing Materials, include the following about sizing: As little sizing shall be used in the fabric as necessary for its proper manufacture. Assuming an average content of natural

*Hart Products Corp.

oil and waxes indigent to the cotton of 3.2 per cent, the total percentage of sizing and natural oil and waxes shall not exceed that given below for each type of fabric:

Sheetings	8.5%
Drills	11.0%
Sateens	10.25%
Broken twills	8.15%

PREPARING OF SIZE-MIXTURES

Procedure.—The following is the actual procedure in use at one of the mills: The water in a standard 42-inch size-kettle is brought to a level of 29 inches and the starch and compounds (exclusive of the tallow) are added. The mixture is stirred cold for 10 minutes and then heated by turning the steam on gradually so that the boiling point is reached within 30 minutes. It is then cooked for 1 hour and 30 minutes at 204° F, the tallow added, and the mix boiled for another 15 minutes. In this mill it was found necessary to add finally from 1 inch to 3 inches of water in order to obtain the standard level, which was set at 38 inches. After the water is added, the batch is again brought to a boil, after which it is ready for use.

Quality of Water.—Water for the cooking of starches for slashing should approach the purity of distilled water as nearly as possible. In several instances where the starch was "going to water" it was found upon investigation to be due to water contaminated with sufficient heavy chemicals to destroy the body of the starch-paste completely. The addition of cold water to the boiled paste is in any case to be avoided inasmuch as it has a tendency to congeal the size and produce lumps that are difficult to get back into perfect mixture. The addition of cold water after the size is made tends to make an uneven size. If it is necessary to add water to dilute the size, only hot water should be used. If nothing but cold water is available, it should be added in such a small stream that it will rapidly warm up before it has an opportunity to congeal much of the size.

Addition of Softeners.—There are two prevalent methods of adding the ingredients other than starch to the mix. One method is to add them at the start with the starch; the other, after the starch has been cooked. One mill has tried a number of methods of adding the auxiliary sizing materials and finds no objection to adding all the ingredients with the starch except raw tallow, which is preferably added after the mix is cooked. Tallow and other fatty materials, particularly if they are not soluble or self-emulsifying, seem to interfere with the bursting and proper gelatinization of the starch granules, causing a non-uniform lumpy size, varying with the amount of stirring, cooking, and concentration of the mix. It has been found to be more advantageous to add such raw softeners either after the starch-paste has reached the boiling point, or 10 to 15 minutes before the termination of the cooking of the batch. At that stage, the fat can no longer interfere with the pasting of the starch and ample time is still allowed to thoroughly emulsify the fat with the starch.

Addition of Antiseptics.—If a separate antiseptic is used, it is better added at the completion of the cooking, so that it may exert a minimum effect on the starch and, if it is volatile, the loss will be reduced to a minimum.

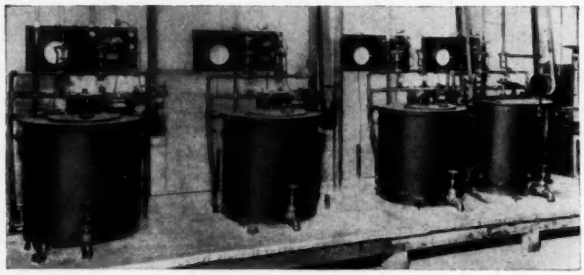
Temperature in Size Box.—Temperatures in the sow-box may vary from 170°F. to 210° F, depending upon construction of the warp and conditions in the mill. The higher temperature has the advantage of giving better penetration, though it may have a greater tendency of thinning out the size and so give a smaller size take-up. Some advantages in tensile strength and improved weaving-properties of the yarn have been claimed for sizing at lower temperatures, viz. about 170° F. At the latter temperature, it is stated there is less degradation of the starch and also a greater take-up of size by the yarn, due to the thickening of the starch-paste. It is generally conceded, however, that better sizing is obtained by keeping the temperature in the size-box as high as possible. In one set of experiments on 22s yarn, there was a definite increase in breaking strength as the sizing temperature was increased. This is shown in the following table:

Temperature of Size Box °F.	*Ends Broken, per Yard of Cloth*	*Breaking Strength* oz.	*Gain* %
Unsized yarn	....	10.03	.....
171	0.77	12.76	27.21
197	1.07	13.19	31.50
207	1.13	13.46	34.19

Time of Cooking.—As has already been mentioned, prolonged cooking and agitation break down the starch sacs, causing a thinner starch-paste. The more the granule-covering is disintegrated or fragmentized, the thinner the paste; the most fluid paste for a given starch is obtained when the covering becomes completely soluble or nearly so. The disintegration of the sacs and consequently the drop in the viscosity or body of the paste is most pronounced at first, but finally reaches a stage when further processing produces comparatively small changes. Evidently the starch-paste at this stage is best adapted for the most uniform sizing. The amount of cooking and agitation required to reach that stage varies with different starches and with the same starch depending upon the method of preparing its paste. There are consequently many opinions as to the time required to cook a given starch to obtain the best results.

The usual mill-practice is to bring the starch-mixture to a boil within 20 to 30 minutes, and to keep it at the boil for a definite period, depending mainly upon the nature of the starch. It is recommended that thick-boiling corn starch be cooked for 1 hour and 15 minutes to 1 hour and 45 minutes; thin-boiling starch, 30 to 45 minutes; potato starch, about 2 hours; sago flour, 2 to 4 hours; and tapioca, the same as corn starch.

Uniformity of Size-Mixture.—The best way to obtain the most uniform size-mixtures is to prepare them in comparatively small batches. The ideal condition is when the kettle of size can be used within an hour from the



Courtesy, Taylor Instrument Companies

Fig. 2—Cooking and Storage Size-Kettles with Full Automatic Temperature Controls.

time it is finished, inasmuch as both stirring and heat have a considerable action on the fluidity of the starch. It is especially detrimental to keep the size-mixture overnight or over the week-end. Some mills manage to produce only the amount of size required for the day and if any is left over at the end of the day it is thrown away. Others prefer to use such material, either as is, or to mix it with fresh size the next day. A starch mixture that has once congealed and is then re-heated is necessarily an inferior size. If size must be stored overnight, it should be kept hot, as gelatinized starch-paste upon re-heating will not have the viscosity, uniformity and smoothness of fresh size.

Temperature Control.—It is generally conceded by mill men that automatic temperature controls on the slasher are essential for best results. Temperature control on the size-kettle permits the gradual, uniform, and duplicable gelatinization and boiling of the size with the minimum attention by the attendant. Temperature control on the size-box tends to give a more uniform size take-up and, on the cylinders, yarn with more uniform moisture content and free from baked size. There is also a saving of steam, as the slashers require only ½ to 2 pounds of steam pressure for efficient operation.

Wetting Power of Size.—Experiments on this subject have shown that raw cotton is capable of being completely wetted-out by hot size. In practice, however, the wetting is dependent to a considerable extent on the application of mechanical pressure, which spreads the size over and forces it into the cotton yarn. The conclusion is drawn that thorough wetting of cotton by size can best be effected by working as near to the boiling point as possible and by taking care that the squeeze-rolls exert effective pressure on the wet yarn.

Stains on Sized Yarn.—Stains arising in sizing may be due to hard size, wet drippings from the hood, or by rusty size. Stains are also caused by burnt starch. In one case this trouble has been remedied by moving the coils in the storage kettle further apart.

PENETRATION OF SIZE

The penetrating power of size into the yarn depends upon many factors, such as the temperature of sizing, concentration and viscosity of the starch-paste, twist and construction of the yarn, the speed of the slasher, amount of immersion of the yarn in the size-bath, the weight and condition of the squeeze-rolls, and the rate and method of drying. The penetration is greater the higher the degree of dispersion of the starch in the size and the lower the viscosity of the sizing mixture.

Degree of Penetration.—It is claimed that penetration is only desirable to the extent sufficient to favor a good anchorage of the film around the warp, rather than to make a rod-like brittle warp, which would lack resiliency and elasticity. The aims of the sizing process should be to paste down the fibers protruding from the body of the unsized yarn; to fill the valleys on the surface of this yarn; to form a tough, elastic, flexible film around the yarn; and for the film to penetrate far enough towards the center to be well anchored. This would result in a smooth heddle and reed action. The much-sought-after quality of elasticity is probably not present in a yarn in which size has penetrated to the very core and surrounded every fiber, while it could well be present where the yarn is merely coated with the size. On the other hand, it is stated that the size must penetrate sufficiently or the size will shed.

SQUEEZE ROLLS

Weight of Rolls.—The first or front squeeze roll helps the penetration of the size and removes the excess from the yarn. The second roll or the one nearest the cylinders, also known as the finishing roll, completes the squeezing of the size into the yarn and prepares the latter for quicker and more uniform drying. The weights of the rolls seem to vary from 320 pounds to 575 pounds, some using the lighter weight for the first roll and others for the second one, although the former method seems to be preferred. On 22s yarn with a twist multiplier of 4.64, 3,000 ends per set, and a cloth construction of 96 x 64, one mill reports the weight of the first roll as 350 pounds and the second, as 500 pounds.

Covering the Rolls.—For good results, the squeeze rolls should be properly covered. One mill-man furnishes the following directions for covering the rolls. The rolls should first be painted with a good lead-paint, undiluted, to prevent rusting. When dry a second coat is applied and, while still wet, the roll is wrapped with about 4 layers of a 64 x 64 sheeting construction. The slasher blankets or cushions, which go on next, should first be shrunk as follows: About 5 yards for the first roll and 6 yards for the second roll are immersed in water at 90° F. and allowed to soak for 12 hours without further heating. The blankets are then carefully put on the rolls. The ends of blankets should not be trimmed for a day or so after they have been put on, but the selvages are tied with strings to prevent splashing of size on the floor.

In the above case a 16-ounce wool blanket was used. In another mill the blanket on the front roll is replaced by 2 pieces of burlap 7 yards in length and on the second roll by 1 piece of burlap 5 yards long, followed by two 6-yard lengths of slasher cloth. Another mill uses 4

(Continued on page 282)

PROCEEDINGS OF THE
American Association of Textile Chemists and Colorists

MAY 18, 1936

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Members should notify the **Secretary** immediately of all address changes

Research Program of the American Association of Textile Chemists and Colorists Receives Renewed Support for the Coming Year

Textile Foundation, Chemical Foundation and Eavenson & Levering Company Continue Appropriations Another Year

AT A meeting of the Directors of the Textile Foundation held in Washington April 15th, reports of the work of the Research Committee of the American Association of Textile Chemists and Colorists during the past year were presented and a request made for a continuance of the Foundation's support during the coming year. As a result of this meeting a grant of $12,500 was voted by the Foundation in order that the work now under way might be continued.

The special projects for which grants were made are as follows: Fundamental Study of Vat Printing Pastes (continuation), The Effects of Oxidizing and Reducing Agents on Wool, and a further study of The Chemistry of Wool Fibers, The Quantitative Determination of Fibers in Mixtures (continuation), The Determination of Oil, Soap and Other Extraneous Material in Wool and Various Stages of Wool Processing.

The confidence which the Textile Foundation places in the work of our Research Committee is extremely encouraging and will serve as a decided stimulus to the efforts which the committee is making to develop research work in this country as regards textile chemistry, dyeing, bleaching, printing and finishing. A statement in regard to the future program of the Textile Foundation and a list of the Directors will be found on page 281 of this edition.

The Chemical Foundation has increased its appropriation to $3,000 for the coming year and the Eavenson & Levering Company renewed theirs of $2,400. These grants are to be used entirely in connection with the work of the sub-committee on The Chemistry of Wool. The work of this committee is discussed in the report of the sub-com-

mittee on The Chemistry of Wool made by Alban Eavenson, Chairman, which appears on this page.

In addition to the research projects already mentioned last year the Textile Foundation appropriated $2,500 to be used jointly with another $2,500 appropriated by the Throwsters Institute for a Study of the Creping of Rayon Fabrics. This work is in active progress at the present time.

The Association will also continue the research work upon the Mercerization of Cotton during the coming year and this will be supported from the funds of the Association.

As a result of this cooperative support mentioned above, the Association's budget for research work during the coming year will be well over $20,000.

LOUIS A. OLNEY,
Chairman, Research Committee.

Report of the Sub-Committee on the Chemistry of Wool

By ALBAN EAVENSON, *Chairman*

THE trend of the research on wool which is being conducted at the National Bureau of Standards for the American Association of Textile Chemists and Colorists is clearly indicated in the evolution of the name of this research sub-committee. Organized about two years ago as the "Committee on Wool Scouring," the title was soon broadened to the "Committee on the Action of Alkalies on Wool," and finally to the present ambitious and comprehensive name. These changes have not resulted from legislation or executive order, but only from an attempt to describe more accurately the work being done by the research associates, Dr. Milton Harris and his assistants, under the direction of the committee. It appears that the present title of the committee will be adequate for some time.

In the report of the committee a year ago* it was stated that "from the chemical viewpoint, wool is a very reactive substance." During the past year further evidence has been adduced to support and interpret this thesis. It may now be stated with considerable assurance that:

(1) Contact of wool with acids, alkalies, oxidizing and reducing agents results in definite chemical reaction.

(2) Even slight chemical changes in the wool protein render the wool fiber more susceptible to deterioration or damage in subsequent processing or use.

(3) This chemical action and incipient damage is generally not revealed by the usual physical tests, but may be detected by chemical means.

Three research papers† are being published at this time by Dr. Harris and his associates, Dr. J. A. Crowder and Mr. Arthur Smith. These articles contribute further important information regarding the nature and mechanism of the chemical changes which obtain when wool reacts with alkalies and with oxidizing agents. There are also described practical means which have been developed to detect and evaluate this chemical action.

Two of these papers report studies on the oxidation of wool and deal more specifically with the effect of hydrogen peroxide. In the report last year it was stated: "Previous treatment of wool with either oxidizing or reducing agents increases the rate of sulfur removal when the wool is treated with alkaline solutions." The new results show further that although wool may be apparently undamaged by a peroxide bleach, showing no change in compressional resilience or in wet breaking strength, yet the cystine content of the wool is considerably decreased and the wool is rendered much more susceptible to subsequent damage by alkaline solutions. The extent to which wool has been oxidized may be determined quantitatively by measuring the related decrease in its cystine content or the increase in its alkali solubility. The degree of oxidation of wool in hydrogen peroxide solutions increases with concentration of the peroxide, showing a most pronounced increase above 4-volume solutions. The injurious effect of hydrogen peroxide also increases with time of treatment, with temperature and with the pH (above 7) of the solution. A temperature of 50° C. is critical for a 2-volume solution.

It is also pointed out that many operations in the processing of wool involve, or may be accompanied by, oxidation of the wool protein. Oxidation of wool also occurs in the normal atmosphere, influenced by conditions of light, temperature and humidity.

As a consequence of this information it is obviously desirable that the manufacturer should know whether or not a particular lot of wool or piece of cloth has been previously treated with hydrogen peroxide or other oxidizing reagents. Available physical tests and dyeing tests are not specific for this purpose. A simple qualitative test, using lead acetate, has therefore been developed for this determination. However, as shown in the research paper, this test must be conducted under controlled conditions in order to obtain dependable results.

The third paper of this group deals with the mechanism of the alkali degradation of wool, with particular reference to the fundamental chemistry of sulfur in the protein. It has been shown in previous papers by Dr. Harris that the primary attack of alkali upon wool occurs at the S-S linkage in cystine, apparently the most vulnerable point in the protein molecule. Part of the sulfur is split off as H_2S, appearing in the solution as sodium sulfide, the remainder of the sulfur (about one-half) being converted to a relatively stable form in a different state of oxidation. Experimental evidence in this paper indicates that alkaline hydrolysis of wool results in the formation of a sulfhydryl

*American Dyestuff Reporter, *24*, 315 (1935).

†The first two papers were published in the Proceedings for April 6th; the third appears on page P264, this issue.

derivative and a sulfenic acid. The latter is unstable in alkaline solution and immediately decomposes into an aldehyde and hydrogen sulfide. As stated in the earlier report, any knowledge relating to the chemistry of sulfur in wool protein is also of immediate interest and value to investigators in the fields of biology and medicine.

Yours very truly,

Wm. D. Appel, Textile Section, National Bureau of Standards.

Hugh Christison, Chemist, Arlington Mills.

Dr. Milton Harris, Research Associate, National Bureau of Standards.

G. E. Hopkins, Technical Director, Bigelow-Sanford Carpet Co.

Dr. H. A. Neville, Professor of Chemistry, Lehigh University.

Dr. Donald H. Powers, Chemist, Rohm & Haas Co.

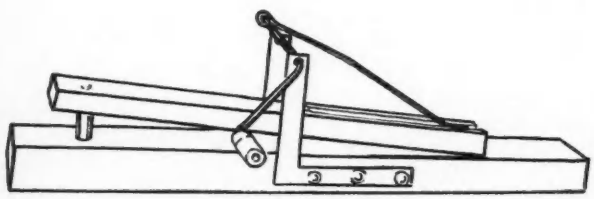
Dr. Robert E. Rose, Director, Technical Laboratory, E. I. du Pont de Nemours & Co.

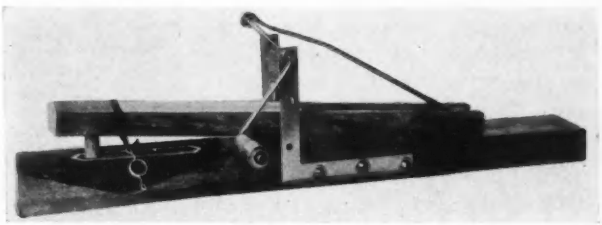
Dr. Werner von Bergen, Chemist, Forstmann Woolen Co.

Alban Eavenson, *Chairman,*
Committee of the A.A.T.C.C.

The Durfee

Crock Testing and Recording Machine*





EVER since its beginning the American Association of Textile Chemists and Colorists through its Research Committee has been working towards the development of exact standards for the testing of dyed textiles. It is believed that the following details of the new standard Crock Meter will be of interest.

Crocking or rubbing tests have long been the cause of disputes. Some people crock hard, some people easy. The dyer or seller cannot tell if the same cloth will please the agent, selling house, or purchaser today or tomorrow. The chemist cannot tell if his process is a little worse or a little better, because the test is uncertain and he can't be sure.

The Research Committee has had for some years a Sub Committee on Crocking of which Dr. Hans Meyer is chairman. The matter seemed more and more important until finally machines for definite results began to be made. One of these seemed cheap enough for general use and was quickly taken up at the suggestion of Professor Olney. This machine, which was designed by Mr. Walter C. Durfee, is illustrated in the picture. It makes crock records on 2" by 2" squares of cotton, which are held by a ring on the crocking finger of the machine.

These are very definite, and widely admitted to be definite, and very useful. The records are clipped to the goods; or otherwise kept. It makes a definite referee between the dyer, agent, seller, buyer, etc.

The first design was made hastily for use in the laboratory of the W. C. Durfee Co., Inc., and rapidly improved by consulting with various textile people.

This machine, which has been accepted as the standard for the American Association of Textile Chemists and Colorists by the Research Committee, has a round finger of diameter 5/8 inch, length of stroke four inches, and a force on the crocking finger of two pounds. Unsized white cotton cloth is specified for the tests. (The Committee tentatively suggests 20 double strokes as the most useful for comparison tests between dyer, chemist, agent, and buyer.)

These crock recording machines, "Crock Meters," may be purchased directly from the Association, care of Lowell Textile Institute, Lowell, Mass., New York City, or from the makers, W. C. Durfee Co., Inc., 114 Federal Street, Boston, Mass. The price is $10 postpaid.

*A further article on the technical features of the development of this device is being prepared and will be published at a later date.

Proceedings of the American Association of Textile Chemists and Colorists

The Mechanism of Sulfur Lability in the Alkali Degradation of Wool Protein

By J. A. CROWDER and MILTON HARRIS*

It is the purpose of this paper to describe the behavior of sulfur in wool under conditions which are very different from those ordinarily used in studies on sulfur lability and to point out a probable mechanism by which sulfur is split from wool during alkaline treatment. The data indicate that the primary process in the alkaline cleavage of the disulfide linkage consists of a hydrolytic rupture of the disulfide group with the formation of a sulfydryl compound and a sulfenic acid. The sulfenic acid is extremely reactive and unstable in alkaline solution and immediately loses hydrogen sulfide and forms an aldehyde. The results of the investigation indicate that the existence of labile-sulfur in proteins is not an indication that the bulk of the sulfur is present in more than one form.

I. INTRODUCTION

THE lability of sulfur in cystine and cysteine and their derivatives, and in various disulfides, mercaptans and proteins has recently received much attention. Excellent reviews and bibliographies on the voluminous literature on this subject are recorded in the papers of Gortner[1] and Clarke[2] and their collaborators and for that reason need not be discussed here.

Labile sulfur is an arbitrary name given to that portion of the sulfur which splits off from sulfur-containing substances on treatment with various alkalies or with alkaline solutions of various reagents such as lead acetate, lead nitrate, etc. It is obvious that the value obtained for the amount of labile sulfur will depend on the method used and the specific conditions of treatment. There have been postulated several mechanisms, which will be discussed later, for the splitting of sulfur from cysteine, cystine and other mercaptans and disulfides. In the case of proteins, however, results which have appeared to be anomalous have led a number of investigators[3] to assume the existence of a number of sulfur combinations in proteins.

The results of the present investigation make it unnecessary to assume that the existence of labile sulfur in proteins is an indication that the bulk of the sulfur is present in more than one form. It is the purpose of this paper to describe the behavior of sulfur in wool under conditions which are very different from those ordinarily used in studies on sulfur lability and to point out a probable mechanism by which sulfur is split from wool during alkali treatment.

II. EXPERIMENTAL PROCEDURE

Purified wool yarn, the preparation and properties of which have been described elsewhere[4] was used in this work. The alkali treatments were performed in a 2-liter filtering flask, fitted with a dropping funnel for passing liquid into the flask and having the side-neck connected to a suction pump for removal of the liquid. The flask was immersed in a water bath at 65° C. During the treatments, every precaution was taken to keep oxygen out of the reaction mixture. A 6-gram sample of wool was placed in the suction flask and the air exhausted and replaced with nitrogen. 600 ml. of a 0.05 N solution of sodium hydroxide, previously boiled to remove dissolved air, was then added. The flask was shaken frequently. At the end of each treatment, the supernatant liquor was drawn off and the wool washed by running freshly distilled water through the flask until the washings were no longer alkaline to phenolphthalein. The water remaining in the flask was drawn off and the wool was partially dried under reduced pressure at 65° C. for 2 hours. The wool was then rapidly transferred to a vacuum desiccator where it was dried to constant weight over calcium chloride. After drying, all samples were stored in an atmosphere of nitrogen.

III. RESULTS AND DISCUSSION

Samples of purified wool were treated as previously described for varying periods of time. The loss in weight of the wool and the sulfur and cystine content of the alkali-treated wool are given in Table 1. The results* are in good agreement with those obtained previously[4] although no precautions were taken to exclude oxygen in the earlier experiments.

The data indicate a rapid splitting off of a portion of the sulfur during the early stages of the treatment. After about four hours the sulfur content approaches a constant value which is not significantly changed on further treatment.

*Research Associates at the National Bureau of Standards from the American Association of Textile Chemists and Colorists.

*In comparing the values obtained in the present work with those in the earlier experiments, it should be noted that the data in this paper are calculated on a dry-wool basis while those in the previous experiments were based on the weight of the conditioned wool.

TABLE 1

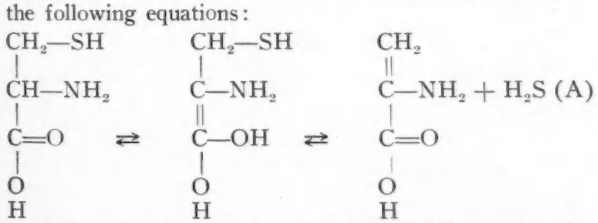
Effect on Wool of the Continued Action of 0.05 N. Solution of Sodium Hydroxide at 65° C.

Time of Treatment	*Loss in Weight*	*Alkali-treated Wool — Sulfur Content*	*Alkali-treated Wool — Cystine Content by Sullivan Method*
Minutes	Per Cent	Per Cent	Per Cent
0	0	3.72	13.40
15	2.27	2.91	6.91
30	3.52	2.56	4.85
45	4.67	2.35	5.13
Hours			
2	6.40	2.24	4.41
4	9.38	2.13	3.70
8	15.21	2.03	2.64
46*	61.50	2.28	2.65

*The samples became gelatinous and a portion of the fiber was lost during washing. The accuracy of these values is questionable.

The conditions under which these experiments were carried out; namely, the temperature and concentration of the alkaline solutions and the duration of treatment, are very mild compared with those generally used in determining the labile sulfur in cystine, cysteine or their derivatives. The extreme ease with which approximately one-half of the sulfur is removed from wool under such comparatively mild conditions suggests that the first step in the alkali degradation of wool is a splitting of the disulfide linkage into one labile and one comparatively stable sulfur group.

Two mechanisms for the sulfur lability in cysteine and its derivatives and in disulfides have been recently advanced by Nicolet[5] and by Schöberl and Wierner[6]. The former suggests that the removal of sulfur from cysteine by alkalies takes place as a 1, 4-elimination of hydrogen sulfide from an intermediate enolized form according to the following equations:



He also suggests that from cystine, RSSH or eventually H_2S_2, would split out.

Schöberl and Wierner studied the alkaline cleavage of disulfides and found evidence that the primary process in the cleavage of aliphatic disulfides of a definite type consisted in a hydrolytic rupture of the disulfide linkage with the formation of a sulfydryl compound and a sulfenic acid according to the following scheme:

$$RCH_2—S—S—CH_2R \rightarrow RCH_2SH + HOSCH_2R \quad (B)$$

The sulfenic acid, being extremely reactive and unstable in alkaline solution immediately loses H_2S and forms an aldehyde according to equation (C). They also postulate that in the

$$RCH_2SOH \rightarrow RCHO + H_2S \quad (C)$$

presence of air, the sulfydryl groups will be reoxidized to disulfide groups after which the reaction in equation (B) would again take place. Even though air were not excluded during the alkali treatment of wool, it would be very doubtful as to whether such a reaction might take place, since the sulfydryl groups are held in fixed positions in the wool molecule and would thus be kept from recombining.

The experimental evidence in the present investigation indicates that the alkali degradation of wool proceeds according to equations (B) and (C). When the alkali-treated samples were tested for aldehydic properties with Schiff's reagent, it was found that an intense violet-red color was formed on the wool in a few seconds, while the untreated wool was colored only a faint pink by the same treatment. Similarly the alkali-treated samples gave positive sulfydryl reactions with ammoniacal sodium nitroprusside solutions while tests on the untreated wool were negative. It can also be easily demonstrated that the sulfur which is split off from the wool is in the form of inorganic sulfides. If an aliquot of the mother liquor from the alkali treatment is saturated with bromine and heated on a steam bath for one-half hour, the sulfur is oxidized to sulfate and can be determined as barium sulfate. It has been shown that the sulfur in wool or in cystine is not oxidized to sulfate under these conditions. The losses in sulfur of the wool, calculated from the sulfur contents of the alkali-treated samples and also from the sulfur found in the mother liquor are given in Table 2.

TABLE 2

Loss of Sulfur from Wool Resulting from the Continued Action of 0.065 N Solutions of Sodium Hydroxide at 65° C.

Time of Treatment	*Loss in Sulfur — Calculated from Residual Wool*	*Loss in Sulfur — Sulfur Found in Mother Liquor*
Minutes	Mg./Gram Wool	Mg./Gram Wool
10	4.4	4.0
20	8.8	7.4
30	10.1	9.7
40	10.4	9.8
50	10.9	10.2
Hours		
1	11.6	11.3
2	12.8	12.1
3	14.0	13.6
4	14.5	14.0
5	14.9	14.8

It has been previously mentioned that under the conditions of these experiments, cysteine and its derivatives would be comparatively stable. That the sulfur in the

cysteine in wool (obtained by reducing wool in alkaline solution) is stable under these conditions is readily shown by treating wool with 0.05 N of sodium hydroxide solution containing 1 per cent of sodium sulfide. After 2 hours' treatment, the wool loses about 5 per cent of its sulfur whereas in the same treatment with no sodium sulfide present, wool loses about 40 per cent of its sulfur.

It is apparent that since the wool is not in solution, not all of the disulfide groups will react with alkali simultaneously. It is probable therefore that sodium sulfide, which is immediately formed by the action of the sodium hydroxide on some of the disulfide groups, will tend to reduce unreacted disulfide groups to sulfydryl groups and make them more stable towards the alkali. On the basis of this, it follows that if the sodium sulfide is removed from contact with wool as rapidly as possible, the sulfur content of the residual wool should be lower than that of wool which is allowed to remain in contact with the sodium sulfide. In order to test this 5- and 12-gram samples of wool were placed in 400 ml. flasks and a 0.05 N solution of sodium hydroxide solution at 65° C. was allowed to flow continuously into the flask so that the wool was in practically constant contact with fresh alkali. After 4 hours' treatment, the samples were washed and dried as previously described and analyzed for loss in weight and sulfur and cystine contents. The results are recorded in Table 3 and are compared with results obtained on a regular 4 hour sample (Table 1). The data constitute further evidence that the labile sulfur comes from the formation of a sulfur compound other than cysteine and that cysteine is relatively stable under the conditions of these experiments. It is also of interest to note that in treatment No. 4, the 50 per cent splitting off of sulfur that would be expected under ideal conditions is closely approached.

While qualitative evidence is readily obtained which indicates the presence of sulfydryl and aldehydic groups in the alkali-treated wool, tests for the presence of those groups in the hydrochloric acid hydrolysate obtained in the analysis for cystine were definitely negative. However, when the reactivity of the aldehydic and sulfydryl groups formed in the hydrolysate is considered, it is not surprising that negative tests were obtained. Under the conditions of the hydrolysis, namely, 6 N hydrochloric acid at 120° C. for 9 hours, it is very probable that recombination between the aldehydic and sulfydryl groups may take place. A suggested mechanism for such a reaction would be the formation of a thioacetal. To test for the formation of stable thio-compounds hydrolysis was carried out in 18 N sulfuric acid. Acid of this strength is known to cleave thio-compounds which are stable to more dilute acids. The results in Table 4 show that the values obtained by use of 18 N sulfuric acid are definitely higher than the values obtained with 6 N acid. The somewhat higher values for cystine obtained by the Folin-Marenzi method are in accord with results obtained by other investigators and may be attributed to lack of specificity of the Folin-Marenzi reagent. It may be concluded, however, that a more stable thio-compound is formed in the dilute acid hydrolysate*.

TABLE 3

Comparison of the Effect on Wool of Standing and Flowing Baths of 0.05 N Solutions of Sodium Hydroxide at 65° C., the Time of Treatment Being 4 Hours

Treatment	*Loss in Weight*	*Sulfur Content*	*Fraction of Total Sulfur Lost*	*Cystine Content*
	Per Cent	Per Cent	Per Cent	Per Cent
(1) None	...	3.72	...	13.4
(2) Regular standing bath (From Table 1)	9.4	2.13	42.7	3.7
(3) 45 liters of alkali flowed over 12 g. of wool..	14.4	2.02	45.7	2.6
(4) 45 liters of alkali flowed over 5 g. of wool...	14.3	1.92	48.4	2.5

*There is also a possibility that some of the sulfydryl formed in the wool during the alkaline treatment may react to form a stable thio-compound even before hydrolysis. Further investigations are now in progress.

IV. REFERENCES

[1]J. Am. Chem. Soc. *44*, 341 (1922); J. Biol. Chem. *72*, 433 (1927); Ibid. *83*, 681 (1929).
[2]Ibid. *89*, 399 (1930); Ibid. *94*, 541 (1931); Ibid. *106*, 667 (1934).
[3]J. Biol. Chem. *9*, 439 (1911); Ibid. *83*, 681 (1929); Bol. Laniera *43*, 992 (1929).
[4]J. Research N.B.S. *15*, 63 (1935).
[5]J. Am. Chem. Soc. *55*, 3066 (1931).
[6]Ann. Chem. *507*, 111 (1933).

TABLE 4

Cystine Analysis of Alkali-Treated Wool Using 6 N and 18 N Sulfuric Acid for the Hydrolysis

Time of Treatment	*Sulfur Content*	*Cystine Content Sullivan Method*		*Increase in Cystine Content*	*Cystine Content Folin-Marenzi Method*		*Increase in Cystine Content*
		6 N H_2SO_4	18 N H_2SO_4		6 N H_2SO_4	18 N H_2SO_4	
Hours	Per Cent	Per Cent	Per Cent	Per Cent	Per Cent	Per Cent	Per Cent
Untreated	3.72	13.3	13.0	— 2	13.2	13.0	— 2
4*	2.02	2.2	3.1	+41	3.6	4.6	+28
8	2.03	2.6	3.5	+35	2.9	3.6	+24

*Sample No. 3 (Table 3) which was treated with flowing alkali solution.

Surface Chemistry and Dyeing*

By HARVEY A. NEVILLE†

CONCERNING the subject of dyeing as an art and as a science, there are probably more conflicting theories, more erroneous statements, and more really wild ideas expressed than can be found relating to any other single subject, with the possible exception of economic theories on the cause and cure of depressions.

If all the theories about dyeing were laid end to end, they would not reach any logical conclusion. In that sense they resemble the statement about economists—if all economists were laid end to end, it would be a good thing.

Furthermore, a diligent search among the chemists of this country would probably have revealed few if any who have a lesser practical knowledge of dyeing than your speaker. I am even ignorant of the names of more than perhaps half a dozen common dyestuffs. In that respect I am like the young lady who said she knew only two words of Spanish, "manana", meaning tomorrow, and "pajama", meaning tonight.

The difficulty of arriving at any comprehensive theory of dyeing, of course, as you realize better than I, is due to the many variables which enter into the dye operation. To mention a few of these, there is the chemical nature and reactivity of the fiber; the physical condition of the fiber, including hydration, swelling, and surface electrical charge; the chemical nature and reactivity of the dyestuff and its physical condition, including especially its degree of dispersion and electrical charge; the temperature, the amount of agitation; the conditions in the dye bath or medium, including the hydrogen-ion concentration, or pH, the presence of salts, wetting agents, and various other substances. Many other variables enter. You might even add to the list such things as the phases of the moon and the disposition of the dyer. It seems almost hopeless, then, to say anything about dyeing that will be universally true.

However, in a broader sense, it must be true that some of the general principles which have found acceptance in related fields must have some application to dyeing, and it is in this respect only that I am interested in the subject of dyeing—as a problem of bringing two surfaces together, making them stick, and perhaps producing a permanent combination.

We are dealing in the case of fibers and dyestuffs with materials in a highly dispersed condition, that is, with two materials in which the ratio of surface to volume or mass is very great, and in such systems the properties of the surface become the predominant properties of the material. There are known principles which determine, to a limited extent at least, the application of something to a surface and the removal of something from it. I hope by means of the slides which I shall show you to outline these general principles. Then if it can be indicated how these apply to dyeing, perhaps you may find an excuse for the title of this talk.

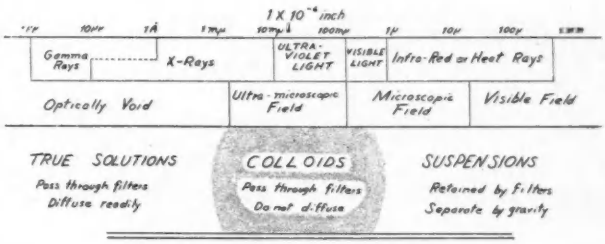


Fig. 1

The first few slides offer a review of elementary colloid chemistry. In Fig. 1, at the top, there is a logarithmic scale to indicate that what is commonly known as the colloidal range falls roughly between a millimicron and perhaps one-half micron. Particles having diameters within this range are not usually directly visible—that is, they are below the microscopic field.

In Fig. 2 it is shown by a diagram that particles having diameters within the colloidal range have the property of scattering light. The intensity of the scattering is inversely proportional to the fourth power of the wave length of the light, consequently the short waves are much more scattered than the longer waves. The blue, being of shorter wave length, is scattered more than the red, and if a beam of white light passes through a medium containing material in the colloidal degree of dispersion, blue light is scattered principally at right angles. If the blue is scattered out, the light which passes through is mainly red.

That principle accounts for many of the color phenomena of nature. It is referred to as Tyndall blue, structural blue, or the blue of turbid media. It may be a disappointment to you to discover that the blue of eyes, about which the poets have written at length, is merely the blue of turbid media. So the blue of the skies, the blue of

*Presented at meeting, New York Section, November 22, 1935.
†Associate Professor of Chemistry, Lehigh University.

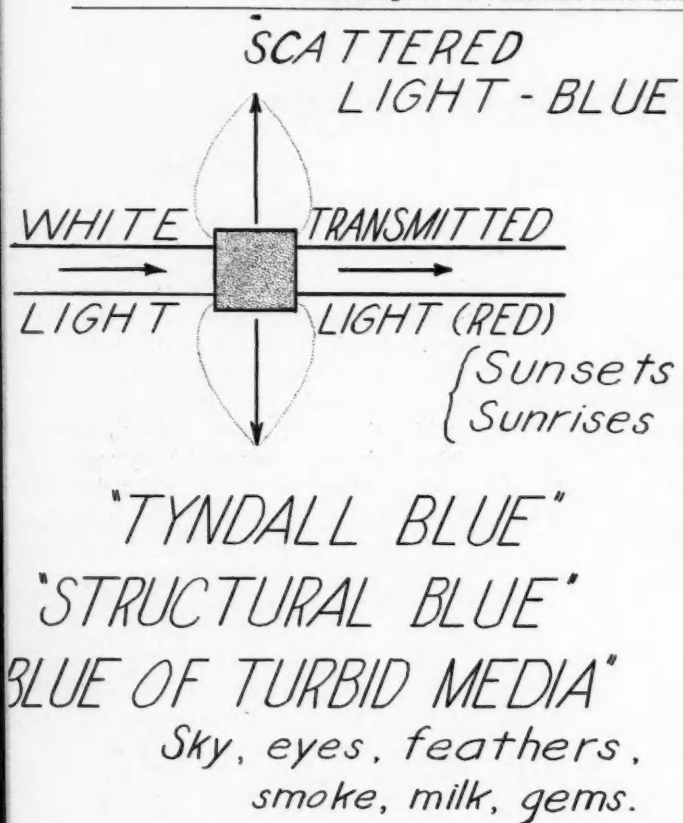


Fig. 2

bird feathers, the blue of cigarette smoke, of skimmed milk are all due to the Tyndall effect.

You see it here in this beam of light. If the room were uniformly illuminated, the smoke would probably not be visible there, but from the intense beam of the lantern the light is scattered to you by these individual solid particles of smoke which are actually of colloidal size.

The viewpoint of colloid chemistry or of surface chemistry is much broader than merely that of particles of a certain size. If you consider the three physical states of matter—gas, liquid and solid—it is obvious that you may disperse material in one of those physical states into any one of the others. All gases mix uniformly to form a homogeneous single phase, that is, the dispersion is molecular, so that there are no colloidal systems which are entirely gaseous, but there are eight other possible combinations as outlined in Fig. 3.

We are considering here a high degree of dispersion of two phases which are mutually insoluble. The one feature which characterizes all of these systems is the enormous extent of interface or boundary surface, and that is why we are justified in using the term "surface chemistry". It was suggested earlier that when material is in this state, where the ratio of surface to mass is extremely great, the surface properties are the most important or determining properties in several respects.

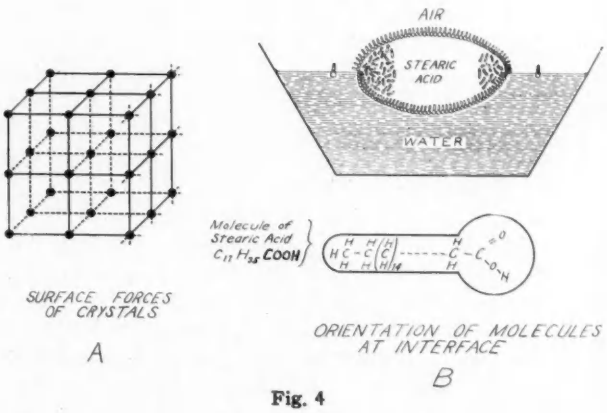


Fig. 4

Fig. 4 is an attempt to illustrate what is meant by surface forces. Fig. 4A might represent a portion of a crystal of sodium chloride within which every sodium ion has

Fig. 3—Types of Dispersed Systems

Dispersed Phase		*Dispersion Medium*	*Illustrations*
Gas	in	Liquid	Fine foam, soap, lather, beer suds, whipped cream.
Gas	in	Solid	Meerschaum, lava, charcoal, silicagel, gaseous inclusions.
Liquid	in	Gas	Mist, fog, clouds, gases at critical state.
Liquid	in	Liquid	Emulsions—milk, butter, mayonnaise (oil-in-water type (milk) (water-in-oil type (butter)
Liquid	in	Solid	Solid emulsions, cosmetics, creams, gels.
Solid	in	Gas	Smoke, dust.
Solid	in	Liquid	Colloidal "solutions", gold sols, gelatins, soap, etc. in water. (Lyophilic (Lyophobic
Solid	in	Solid	Pyrosols—some alloys, ceramics, gold in ruby glass, gems.

six chloride ions arranged symmetrically about it. In the sodium chloride crystal a single sodium ion does not belong to any particular chloride ion but shares its forces of attraction equally with six of these. The same can be said of a chloride ion with respect to the sodium ions. But when an ion is at the surface of the crystal it lacks a neighbor and its forces are not completely saturated or balanced. Those which are on an edge are still less saturated, and those which are at the corners have even greater unsaturation.

These forces extending out into the other phase are real forces or reservoirs of potential energy. We evaluate their intensity for liquids by measuring what we call surface tension. Surface tension is merely an expression of this surface energy, and the numerical value of the surface tension is a measure of the degree of unsaturation of the surface. This can be determined for solids by indirect means.

Molecules in surfaces tend to orient or arrange themselves so that the least active portions, the most highly saturated, or the least polar portions of the molecule are exposed. As a result of this orientation the surface energy or surface tension is able to exhibit a minimum value.

In a molecule such as stearic acid, Fig. 4B, there is a long chain consisting of carbon and hydrogen atoms, similar to a hydrocarbon oil, and there is a polar end, the carboxyl group. This group is soluble in water. It is closely related to water. If the non-polar hydrocarbon chain is short, the tendency of the polar end to dissolve in water, the attraction of water for that end, is sufficient to pull the whole molecule in and complete solubility results; for example, acetic and propionic acids are miscible with water in all proportions.

If a long-chain fatty acid is placed on water it will orient to form a surface film with the polar end in the water and the hydrocarbon end sticking out. This film is ordinarily one molecule deep. Molecular orientation can be illustrated conveniently by melting some stearic acid, pouring it on warm water, and then permitting it to cool and solidify. The stearic acid does not spread over the water, but forms a lens. This lens of stearic acid is solid when cool. One surface of it, the lower layer, has solidified in contact with water, and the orientation is such that the surface consists of polar carboxyl groups. The other side has solidified in contact with air, and the exposed portion consists of hydrocarbon chains.

If the lens is now picked from the surface of the water and dried with filter paper, a drop of water placed upon the upper surface will not spread. Water does not wet that kind of surface.

If the solidified lens is turned over and a drop of water is placed on this other surface, the water spreads out. This is a different kind of surface; it consists of carboxyl groups for which water has a great attraction.

That is a simple little experiment which demonstrates the reality of molecular orientation and of the difference in the wetting of surfaces, even for a single pure material. It shows that orientation of the molecules is able to occur even in opposition to crystal forces.

With this general review we now come to our actual subject—the relation of surface properties to dyeing. By "surface" is meant the boundary where any two phases are in contact—any two immiscible phases, a solid in contact with air or with a liquid, or a liquid in contact with air, or two liquids or two solids in contact. Any surface or interface is the seat of potential energy, surface energy. An interface is also usually the seat of an electrical potential. That is, there is a potential difference between the two phases at the point of contact. This is equivalent to saying that there is an electrical charge upon one of the phases.

Some substances may under certain conditions have a positive charge, and under other conditions a negative charge. One of the most important factors determining the nature of that charge is the hydrogen-ion concentration, which is commonly expressed as pH value.

The pH value is the logarithm of the reciprocal of the hydrogen-ion concentration expressed in gram molecules per liter. At the moment it is necessary to remember only that a pH value of 7 represents neutrality, characteristic of pure water, that numbers below 7 show increasing acidity, and numbers above 7 show increasing alkalinity.

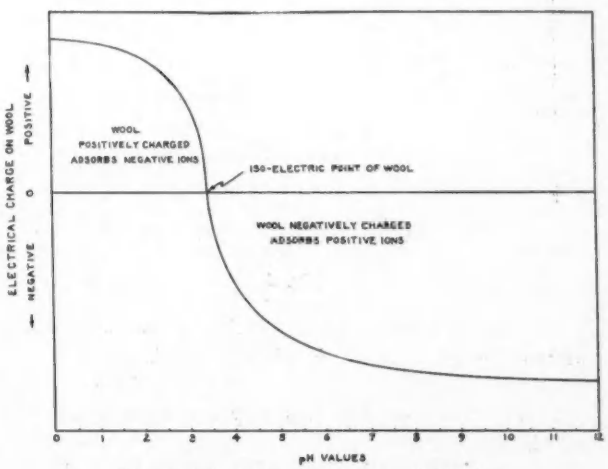

ELECTRICAL CHARGE ON WOOL
POSITIVE
0
NEGATIVE
WOOL POSITIVELY CHARGED ADSORBS NEGATIVE IONS
ISO-ELECTRIC POINT OF WOOL
WOOL NEGATIVELY CHARGED ADSORBS POSITIVE IONS
0 1 2 3 4 5 6 7 8 9 10 11 12
pH VALUES

Fig. 5—The Potential Curve of Wool

The surface potential of wool in contact with solutions of varying acidity up to the alkaline range changes as shown in Fig. 5. In rather acid solutions wool is positively charged with respect to the water. The charge decreases as the acidity decreases, and at a point corresponding to a pH of about 3.5 the potential between the wool fiber and the solution in contact with it is zero. That is called the isoelectric point of wool, and if we go

farther toward the alkaline side the wool becomes negatively charged. Now, if the surface of the wool is the seat of a positive charge in relation to the solution, you can see that this surface will have a great attraction for negatively charged particles, colloidal particles, or even negative ions. We know that the ordinary ions of electrolytes, such as sodium ions and chloride ions, are not highly adsorbed, but that organic ions are adsorbed to a much greater extent. Organic ions are the effective agents in soluble dyestuffs, in wetting agents, in soaps and other detergents.

In the other region the wool is negatively charged and selectively adsorbs positive ions or colloidal particles.

This electrical potential at the surface, it seems to me, must be a very important factor when something is to be added to the fiber or when it is attempted to remove something from it. The problem of adding something to the fiber includes, of course, dyeing, lubricating raw silk in the soaking process, and many other operations. Removal of material from the fiber is illustrated in all the processes of detergency—whether it is in the laundry, or in the boil-off of silk, or the stripping of dyes, or any other process in which something is to be dispersed from the fabric. These two effects are fundamental to most of the operations in the textile industry other than the merely mechanical process of fabrication.

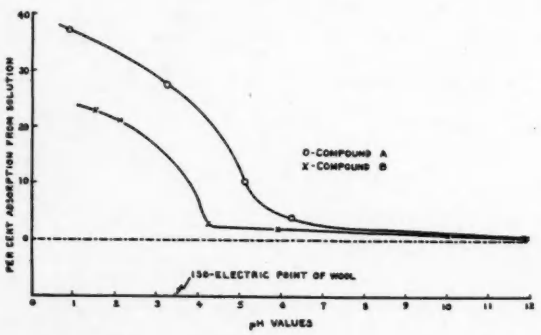


Fig. 6

Some actual data on the adsorption of two well-known wetting agents are shown in Fig. 6. One is Gardinol and the other is Igepon. These curves and the next two were determined experimentally by Mr. Charles Jeanson who is present.

Gardinol is the sodium salt of a sulfated fatty alcohol. The molecule ionizes into the positive sodium ion and a negatively charged organic ion which contains the polar sulfate group. It is this complex negative ion or colloidal particle which is effective in surface phenomena.

If you took the curve in Fig. 5 seriously you would predict that Gardinol and similar substances would be highly adsorbed in acid solution, that is, where the wool is positively charged, and that the adsorption would be negligible in alkaline solutions. This turns out to be the case. The adsorption curves of the wetting agents follow approximately the slope of the potential curve. Of course some adsorption occurs beyond the isoelectric point because of the attraction of matter for matter and the active nature of the materials concerned, but the really considerable adsorption of these wetting agents is in the acid range. From this you can see that it would not be very practicable to employ such wetting agents in solutions of high acidity because they would be exhausted from the bath by wool or silk. Tests have shown that this is the fact.

An acid dye is a substance similar to Gardinol in chemical nature. It is usually the sodium salt of an organic acid. It ionizes in solution into the positive sodium ion and the negative organic color ion or colloidal particle. Thus you would predict that acid dyes would be adsorbed by wool in the manner shown by the previous curve and following the potential curve of Fig. 5.

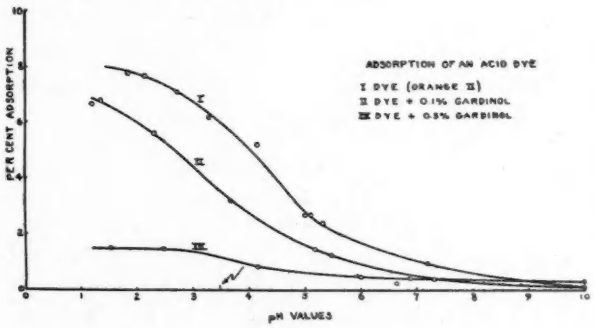


Fig. 7

Curve I of Fig. 7 shows the adsorption of an acid dye, Orange 2. Curve II shows the adsorption of the same dye form the same concentration in the presence of a tenth of a per cent of Gardinol. Gardinol is a substance similar to the dye. It acts here as a leveling agent because the Gardinol is being adsorbed also and to some extent it saturates the attracting forces of the wool, interfering with the adsorption of the dye. Increasing the concentration of Gardinol to one-half per cent (Curve III) cuts down the adsorption of the dye enormously.

Of course it has been known for a long time that acid dyes are most highly adsorbed from acid baths. The explanation, however, has not been so clear until the potential curves for wool and silk were determined. The potential curve for silk is quite similar to that of wool, except that it crosses the isoelectric line at a higher acidity, at about pH 2.3.

With a basic dye you would expect contrasting results. Curve I of Fig. 8 shows the adsorption of Methylene Blue over the pH range. Methylene Blue is a substance in which the colored and adsorbable ion is positive. The other ion associated with the surface-active ion is a simple inorganic ion such as chloride or sulfate. If Gardinol is used with this dye there is an appreciable leveling ac-

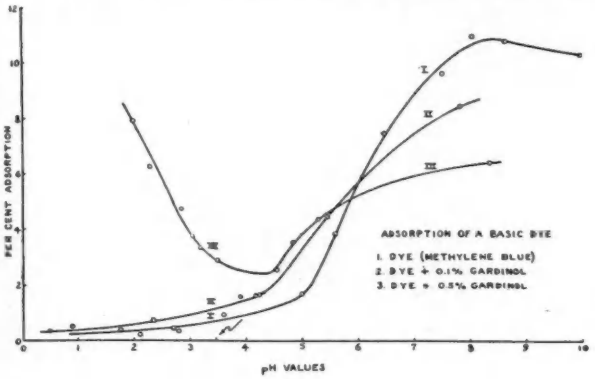


Fig. 8

tion in the alkaline region, but by going over into the acid region, under such conditions that the wool is not apparently dyed by the Methylene Blue alone, it is found that in the presence of 0.5 per cent of Gardinol the wool is dyed quite intensely blue. In this region, instead of acting as a leveling agent for the basic dye, the Gardinol serves as a dye aid.

DETERGENT TESTS

The principles we have been discussing apply equally well when it is desired to remove something from fibers. This is, of course, the reverse of dyeing. Also, it is well to test any theory in both directions if it concerns an equilibrium condition such as adsorption. We have ordinarily assumed that to disperse dirt from fibers a substance is needed which acts as a dispersing or emulsifying agent—something of the nature of soap, something which lowers interfacial tension—and so you do for practical purposes. But in addition to that effect of the soap or similar agent, it appears that the electrical effect of repulsion must have very considerable importance.

Squares of wool cloth were treated with a standard soil and then mechanically agitated in solutions of hydrochloric acid, pure water, and sodium hydroxide solutions of different pH values to determine the effect of the hydrogen ion concentration upon the removal of this soil.

For the lower curve of Fig. 9 there was no detergent, no wetting agent, or substance having the properties of soap. In the experiments for the upper curve, 0.01 per cent of Gardinol was added.

First consider the lower curve. In the acid region, the wool is positively charged. Carbon black, the soil, as you will see from a curve shown later, is always negatively charged. It is not possible to charge carbon black in water positively by any simple means. If the wool is positively charged and the carbon particles are negatively charged, the two attract each other and it is difficult to separate them. When we go past the isoelectric point of wool, the wool is negatively charged and so is carbon. Here we get a repulsion and the farther out in the alkaline

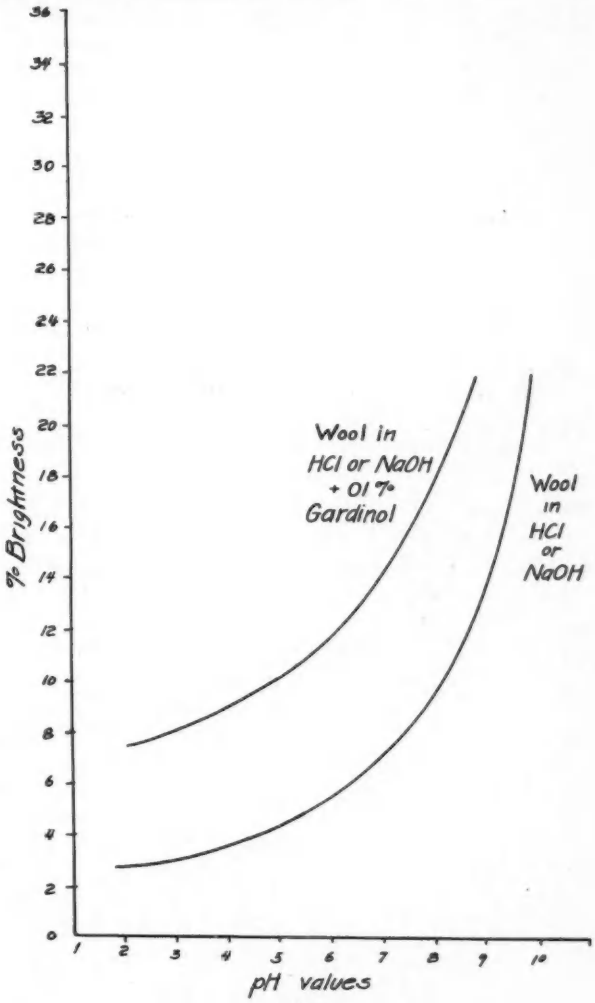


Fig. 9

range we go the greater that repulsion becomes. I have here this series of washed samples ranging from black to a rather light gray.

The numerical values of brightness in Fig. 9 represent the percentage of reflection from the sample as compared to a white magnesia block. Increased brightness, of course, shows a whiter sample. With Gardinol, which can be used in the solutions over the whole pH range, there is an improvement, as shown by the upper curve, but the two curves are parallel. This indicates that even when a detergent such as Gardinol or soap is used, the electrical condition of the surface is really the controlling factor.

Of course soap can be used over only a narrow range in the alkaline region (around pH 10), but it is in this range that detergency should be most efficient from the viewpoint of the electrical relations. It appears that it is practically impossible to do what a number of enthusiasts for soap substitutes have suggested—that is, wash things in neutral or acid solutions. It doesn't seem possible or

reasonable to remove such things as carbon black and oils from fibers in an acid medium, because no matter how active the detergent is, the electrical relations are adverse and the efficiency will be low. We know from practical experience that Gardinol works best as a detergent when used with sodium carbonate or some other alkaline agent. The reason for this is that the soil can be dispersed from the fiber and will not return to it, since in the alkaline range the fiber and soil are both negatively charged and consequently repel each other.

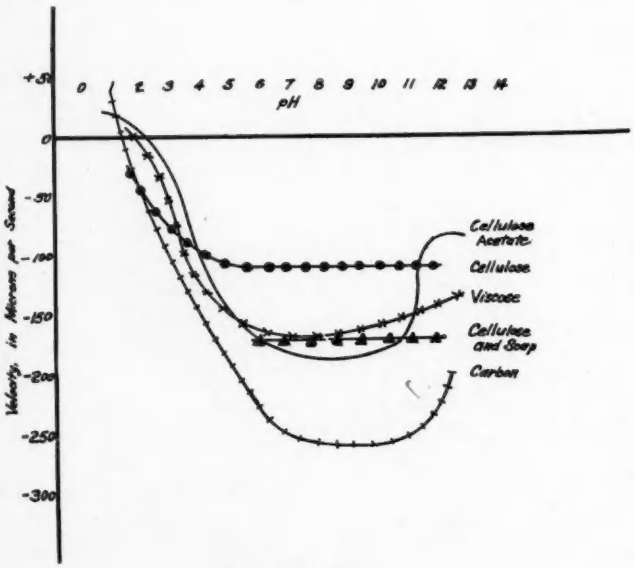


Fig. 10

The curves in Fig. 10 are for the electrical potentials of some other fibers and for carbon black. The curve for purified cotton cellulose shows a zero or negligible charge at about pH 2. It is very difficult to determine the charges in this region where they are very small. The method used is electrophoresis or the motion of the particles in the microscopic field under an electrical potential. There is also the motion of the fluid itself in the little cell, and if the migration velocity of the particles is low, it is very difficult to decide which way they are moving. It is probable that the cellulose does not become positively charged in solutions more acid than pH 2.

With viscose rayon particles the curve is similar, but in the alkaline region they seem to be more highly negatively charged. This is perhaps reasonable, for while the chemical composition is presumably much the same, the surface orientation and activity is probably greater in the regenerated cellulose and it is consequently more highly adsorbent.

Cellulose acetate likewise takes on a more pronounced negative charge in this region. When the pH is increased to about 11, the charge drops back to that of cellulose. This seems to agree with the known behavior of cellulose acetate in highly alkaline solutions. The acetate groups are saponified, the fibers fall to pieces, and cellulose is regenerated.

In the curve for carbon it is shown that the particles become very highly negatively charged in the alkaline range. The pH of a soap solution is normally about 10 and in it would result negatively charged fibers and negatively charged carbon particles with mutual repulsion. Oils are likewise emulsified by soap to produce negatively charged droplets. At very high concentrations of alkali the charge on carbon particles appears to decrease. This is probably not a real effect but only due to the fact that the concentration of ions in the solution has become so high that other effects predominate and interfere with the method of measuring the charge of the particles.

It is also to be noted that cotton fibers suspended in a soap solution, which we can use over this narrow range, have a greater negative charge than when suspended in sodium hydroxide solutions. The negative charge must be due to the adsorption of negative ions. The negative ion in the sodium hydroxide solution is the hydroxyl ion. In the soap solution it is the ion of the fatty acid, an organic ion such as the oleate ion. As a matter of fact, it is really the negatively charged colloidal micelle of the soap solution, consisting of associated soap molecules and the organic anions. These micellae of soap are naturally more highly adsorbed than simple ions and are more effective in producing the negative charge on the particles.

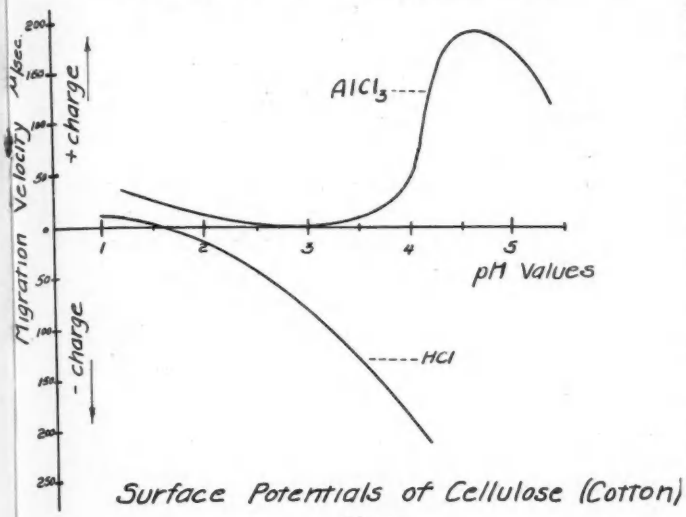
You will note the characteristics of the cellulose materials in a neutral solution in which the number of active positive and negative ions is the same. In pure water, pH=7, the cellulose shows a highly selective adsorption of OH^- ions in preference to H^+ ions. That is easily understood when account is taken of the chemical constitution of cellulose. It has numerous hydroxyl groups in it, and an important principle of adsorption is that like adsorbs like. That is, a substance tends to adsorb the ions which are closely related to its own composition.

MORDANTING

It may be desirable to produce a positive charge on cotton in order to dye it, because the best dyes are acid dyes in which the color ion is negative. If this cannot be done by increasing the acidity, how is it possible? Cotton may be charged positively by applying colloidal particles which bear a positive charge and which are highly adsorbed—for example, colloidal particles resulting from the partial reaction or neutralization of such salts as aluminum chloride—in other words, mordants.

The classical explanation of mordanting is that the mordant is fixed on the fiber and then the dye fixes itself to the mordant. The reasons why this should happen are not obvious. But we can see now, I think, from the standpoint of the electrical relations why and how a mordanting action is obtained. In a solution of aluminum chloride, which is naturally quite acid due to hydrolysis, there

are aluminum ions with a charge of +3 and it might be expected that these would be sufficiently adsorbed to charge the cotton positively. The effect is only slight for such simple ions are not highly adsorbed.



Surface Potentials of Cellulose (Cotton)

Fig. 11

In Fig. 11 the lower curve is part of the potential curve for cellulose in hydrochloric acid. The upper curve in this figure was obtained with aluminum chloride by the addition of hydrochloric acid or sodium hydroxide to vary the pH values. When it reaches a pH of 4.5 enough of the acid resulting from the hydrolysis of aluminum chloride has been neutralized so that colloidal particles of aluminum hydroxide are produced. The particles are not simply aluminum hydroxide but have a very complex composition, a hydrated basic aluminum chloride. The particle has hydroxyl groups in it and bears a positive charge due to the adsorption of Al^{+3} ions or to surface ionization. A single particle has a charge equivalent to perhaps a hundred or a thousand electrons in contrast to the aluminum ion with a charge equivalent to only three electrons.

The maximum effect of this mordant is obtained at about pH=4.5. Farther along toward the alkaline region aluminum hydroxide begins to precipitate and that is not effective as a mordant. That is, at pH values above 4.5 the charge on these colloidal particles is gradually decreased and they coagulate into larger particles which settle out as a flocculent precipitate. In the region of pH=4.5 colloidal basic aluminum chloride has its maximum stability and charge, is highly adsorbed by the cotton fiber, and the latter is positively charged. In this condition the fiber will attract the negative ions or particles of acid dyes.

In this discussion I have attempted to illustrate and emphasize the influences of surface energy and surface potential which obtain at every interface. I have not intended the impression that this is the whole story of dyeing or even necessarily its most important feature. However, by taking proper account of these principles it is usually possible to predict what will happen, or at least the direction in which it will occur, under definite conditions. It is for you to determine the extent to which these considerations can be applied to your practical problems of dyeing.

Here are some samples, not really dyes, but showing pigment effects which may interest you. Of course the particle size of the dye affects greatly its adsorption and the color that is obtained. The degree of dispersion of the dye is another thing that is affected by the pH value of the bath. Here is some Prussian Blue, a blue pigment, and here is dolomite, a white mineral.

If we mix these we expect to get intermediate shades, lighter blues, but the particular shade of blue obtained depends not so much upon the proportions of the two powders as upon the relative size of the particles.

Perhaps you are unable to distinguish them at that distance, but here are three preparations of different shades. This is a light blue, that one is intermediate, and this is a rather dark blue. Each of these mixtures contains one per cent blue powder and ninety-nine per cent white. In contrast, here is a mixture which is thirty-three per cent blue powder and it matches rather closely the intermediate blue containing only one per cent Prussian Blue. Here is a mixture which is ten per cent blue and it is darker by far than the thirty-three per cent blue. In fact you can get almost any shade you wish by varying the relative size of the particles.

It appears that the small particles tend to coat the large ones, and so if you have relatively large particles of white and small particles of blue, you will get the dark blue. If you reverse the condition, and have the white particles smaller than the blue particles, you will get a white.

That same principle is used, of course, in many other fields. In retarding the setting of Portland cement, along with the cement clinker, they grind some gypsum, and since that is a softer material than cement clinker, it grinds finer and coats the other particles, giving a delay in setting, so that the man who wheels the wheelbarrow of cement or concrete to the place where it is to be put has time to set it down and light his pipe and do a few other things before it sets.

In protecting baking powder against going off on the shelf, baking powder being a mixture of sodium bicarbonate and some acid constituent, which will act slowly due to the absorption of moisture, a filler or protector of starch is mixed in, and since the starch is finer grained than the particles of baking soda or acid, it will coat those particles and give protection.

Here are the samples of wool cloth which were washed in the various solutions of acid and alkali, no soap used, and then I have the others with Gardinol, and the same thing was done with cotton, showing similar effects.

I think I should stop now and let Dr. Alexander tell

us if and when any of these things have any bearing on the problems of dyeing.

Thank you. (Applause).

DISCUSSION

Chairman Freedman: I made mention before of having been seated between two conspirators. I should offer my humble apologies and say two learned gentlemen.

The second gentleman I had reference to is Dr. Jerome Alexander, who appeared before us last year and spoke on the nature of combinations between dyes and fibers, and you will recall that he is the author of several books on colloidal chemistry, and is noted as an outstanding authority on that subject. We have asked Dr. Alexander to come here this evening and lead the discussion on this very interesting topic.

Dr. Alexander!

. . . Dr. Alexander asked Dr. Neville a question off the record. . . .

Dr. Neville: Dr. Alexander wants me to talk about Zwitter ions. I will do so as briefly as possible.

How can wool be positively charged under one condition and negatively charged under slightly different conditions? Wool is a protein material and is made up of combined amino acids. A simple amino acid might be pictured as $R\begin{matrix}/NH_2\\ \backslash COOH\end{matrix}$, meaning an organic group with an NH_2 group, which is basic, and capable of combining with a hydrogen ion, and a carboxyl group, which is the acid group, and which can ionize to furnish the hydrogen ion. In an alkaline solution hydrogen ions are removed and the remainder of the amino acid is negatively charged. In an acid solution the hydrogen ion brings a positive charge and the particle as a whole is positively charged.

Now, what is the condition at the isoelectric point? Is it the one of zero charge, as was first assumed, where none of the groups were ionized or combined with hydrogen, or is it the condition of maximum ionization, but an equal ionization in the two directions, that is, where the hydrogen ion from the carboxyl group has gone up on the NH_2 group? Such a particle or substance would be called a Zwitter ion, meaning merely a double ion. If you had an equal number of those groups, you can see that the net effect would be a zero charge, and more recent views are that a protein material at its so-called isoelectric point is a Zwitter ion, or is composed of Zwitter ions entirely.

Cellulose is not an amphoteric material. It does not ionize as an acid and as a base. I think it is not proper to refer to the isoelectric point of cellulose in the same manner, because it is not an amphoteric substance.

Dr. Jerome Alexander: Mr. Chairman and Gentlemen: The complexity of things is shown by the old method of "making" positive and negative electricity. I am going away back to the days of natural philosophers.

If you rub a piece of cat fur over a piece of resin, you get resinous electricity, whereas, if you rub a piece of glass with cat fur, you get vitreous electricity.

One of those electricities was positive and the other negative*, and we are beginning to understand some of these old experiments in the light of the modern electrical structure of matter. Glass and resin give two totally different kinds of electricity. Their surfaces are different. The fur can pull electrons out of one and not out of the other.

In this question of Zwitter ions, and I will try to give you a very commonplace but perhaps appropriate illustration. You have often seen weather indicators, consisting of a little house with two doors. In one door stands a man and in the other door a woman. In good weather the woman comes out and the man goes indoors. When the weather is going to be bad, the opposite situation occurs—the woman retires and the gentleman comes out.

I suppose the Zwitter ion might be considered somewhat along that line. In the presence of acid weather the lady retires and the gentleman comes out, and when the alkaline situation is present, the lady comes out and the gentleman retires. At the isoelectric point, they both stand at the threshold, for the surroundings are just as acid as alkaline.

We have reached the point of view that you can't treat atoms or molecules as homogeneous units. Those of us who are older were taught that an atom was a little spherical particle that you couldn't get inside of. The diagrams modern physicists draw, illustrating what an atom looks like are astounding. Atoms are put down now as mainly empty space. Someone gave this illustration: If you put a tiny shot in New York and regarded that as a proton (the nucleus of the hydrogen atom) and then put a good-sized pea out in Philadelphia, this would represent, in proportion, the distance between the negative electron and the positive nucleus of the atom of ordinary hydrogen. Thus atoms are largely empty space.

When we come to molecules which are built of atoms, a great deal of work has been done by Sir William Bragg and others who are working with the X-ray spectrometer. I brought along some papers of Bragg which give illustrations showing where the atoms are placed in molecules. They have measured with great precision the distance between atoms in a molecule and show just how these atoms are arranged in space. They have also constructed electron contour maps of the whole molecule, which agree with what organic chemists have found out about the same molecules, except that the maps give additional information. I have some of these pictures here and they are very interesting.

Coming now to the question of cellulose and wool fiber, much work has been done on the physical structure of the

*Vitreous was termed positive; resinous, negative.

chemical units, and on how these chemical units are built up into long chains and how these chains are bound together to make a microscopically visible fiber.

We might imagine it somewhat along this line: These pipes in the ceiling are composed of pieces joined together, and each single "length" of pipe represents an individual, elongated, ultimate molecule in the constitution of cellulose. A number of those molecules get joined together by a dehydration process and linked chemically into one long chain, which may run for hundreds of molecules. The bonds linking the individual original cellulose residues into a long chain are definite chemical linkages. However, at the sides of these long chains are residual valences represented in this room by these festoons of paper, which link these long pipe lines into bundles. The paper bonds here are hardly as strong as the screw joints that hold the "lengths" of pipe together, so you can understand how a fiber could be split lengthwise much more readily than it could be broken end for end.

The cellulose diagram shown by Prof. Haworth of Birmingham in his paper before the British Association at its last meeting, shows that the "physiognomy" of the cellulose chains varies as you consider different portions of their long length. Therefore, while we may at times have to consider the charge of the surface as a whole, when we get down to smaller local areas, the local variations of the fiber become an important factor.

Professor Neville made reference to the work of Dr. Wanda Farr. She has brought forward the point of view that these bundles of original cellulose fibers form tiny little microscopically identifiable fiber units which are coated by a pectinous layer that cements them together. She has brought forward evidence that this pectinous layer has a real existence, and is dyed by Ruthenium Red, which is a dye for pectin or pectinous materials, but does not dye cellulose. It would seem that the complexity of the cotton fiber is rather greater than we had thought, and that Dr. Farr's observations add something new which must be considered by dyers.

We speak of permanence of chemical union or the fastening of the dye to the fiber. It makes me think very much of a sign I saw in a beauty parlor: "Permanent Wave, $2; guaranteed six weeks." The idea of permanence there was limited. I mention this to bring out this point that while one set of conditions will cause dye and fiber to come together, another set of conditions may cause them to separate.

If you fill a test tube with kerosene oil, and then immediately pour out the oil and fill the tube with water, the water will displace the oil and wet the tube, because the oil hasn't yet had time to displace the air film and wet the glass. But if you put water in the test tube *first,* that quickly displaces the air, and oil added later will not be able to displace the water. There is a time element involved. If we give the kerosene sufficient time to displace the air, then the oil will hold fast to the tube and the water will *not* wet it.

The question of the oriented adsorption of particles might be brought home to you by the old college song about the boy and the tack:

There was a boy; there was a tack;
There was a teacher new.
The tack sat down upon its head;
The teacher sat down, too.

If the tack had sat down the other way, the dreadful consequences would not have followed. A great deal depends upon which way a molecule points in an interface. (Laughter.)

Dr. Langmuir's assistant, Miss Catherine Blodgett, has been doing some very queer things with the surface fixation of molecules. She can deposit layer after layer, one molecule deep, and pile the layers up one on top of another, just as I have these pamphlets piled one on top of another. Furthermore, by manipulation, which is described in her paper in the *Journal of the American Chemical Society* recently, she can make the molecules all point in the same direction, or she can alternate them in many cases. That is, she will have, say, first a head and then a tail; then a tail and then a head (alternate layers). Or she can have them all facing one way from the surface (continuous layers). It is rather interesting how they are going into the control of surfaces, because surfaces often decide if and how a dye can take hold.

Professor Albert Perrier of Lausame, in pointing out how physists consider the orientation of molecules said: "We talk about molecules and how they are bent or oriented. In order to illustrate to you how this is decided, let us imagine we had a regiment of soldiers, and the soldiers were so small that you couldn't see any one individual. Now, however, suppose that we know that their backs are red and their caps are blue, for example, and that at one moment we could make them all bend in one direction, so that the regiment would look red, and then when we straightened them up, they would look blue." So it is that we deal, in most cases, not with individual molecules, but with large numbers of them and then see what the sum total of the effect is.

Some reference was made by our speaker to the question of dyes being very temperamental. I think he remarked that sometimes the phases of the moon had something to do with it. That brings up a very interesting point of view, because the light of the moon is polarized light, and the notion that the moon has some peculiar effect goes away back into folklore. The word "lunatic" is quite the same as "moon-struck." There is a popular superstition among some people that fish exposed to the light of the moon become poisonous, and somebody or other said—I do not know whether this is correct or not—that polarized light has a rather more profound effect in bringing about decomposition of fish than ordinary light.

About 8 years ago Miss Semmons reported to the British Association work on the effect of polarized light and has made quite a number of claims which have been disputed. I do not wish to decide a moot question of that kind, but I do want to point out that there might be something to the phases of the moon. (Laughter.)

Where there is a widespread popular belief in a thing, there is sometimes something to it. Very often popular beliefs have a foundation. Some British explorers, in one of their books on their early explorations in the Congo, spoke of a silly superstition that the coming of sleeping sickness had something to do with the coming of the tsetse fly. Now, of course, we know that is so. The Nobel Prize was given a few years ago to Dr. Wagner-Januregg who found that general paralysis caused by syphilis could be ameliorated by inoculating the person with malaria. The high malarial temperature seemed to be harmful to the organism that caused the other disease, and the patient could be cured of the malaria by quinine if the proper variety of malaria be chosen.

I read a paper by an Englishman who in former years was the British Government's representative to the Iramba tribe in Africa, and to him came a certain medicine man, who requested that the chief, Kinga, who was suffering from general paralysis, be sent down to a certain malaria-infested district; and the chief did not want to go. The medicine man said to this Englishman, "He will have to go there," and it was the worst malarial spot in Africa. He said that the "pilintu" that causes the paralysis must fight with the "vidudu" that causes the malaria, until the malarial parasite—(he didn't use the term "parasite," but these African words indicate mysterious worm-like or insect-like things)—overcomes the other. "Then," he said, "shall Kinga eat of the bitter roots and be strengthened." They did not have quinine there but they had aconite. This Englishman also found that for four hundred years the natives had knowledge that malaria is carried by the mosquito.

It is perfectly surprising, isn't it, that these "ignorant savages" should have known that; but, of course, observation is not limited to people who study higher mathematics.

I have listened with a great deal of interest to what my good friend, Professor Neville, had to say, and I do think that a study of the principles that he is following up here will throw a great deal of light upon dyeing questions.

I do think, however, that we have to consider certain other practical effects, and I was wondering, Dr. Neville, whether any ultra-microscopic examination has been made as to how these reagents affect the size of the dye particle? The reason I ask that is that in quite a number of cases the addition of acid or the addition of salts will actually cause an aggregation in the dye. Now, of course, when the dye aggregates, you would not expect it to get in or on the fiber so quickly or so well.

There is a question of the change of particle size, which affects the kinetic activity of the particles. The larger the particles are, the less rapidly they move and the less far they can penetrate.

I was wondering whether anybody has followed out this point of view. Most problems in technology, and in science as well, have many different angles, which do not conflict with each other at all. We simply get different points of view of the same phenomena, just as a full-face photograph and profile of the same person will look quite different.

I wonder whether you could tell us anything about that, whether or not there has been any investigation of the question of the effect of change in particle size or aggregation of the dye.

Dr. Neville: I should like to take up Dr. Alexander's points in order if I could recall all of them. I gathered that if you don't believe in orientation of molecules, you should go sit on a tack and be convinced. (Laughter.) When he got down to the matter of putrid fish, I didn't quite see the connection between that and dyeing. I have had people draw red herrings across the trail, but when they bring in rotten fish—

With regard to the illustration of the relative sizes of electrons and protons, it is very apt, and I thought in that connection of the statement of Eddington, that man is mostly empty space. If you could take up all the electrons and protons that make up a man and really bring them up together, they would only fill a glass half full.

Coming to the serious point that was brought up about the particle size of the dye, you realize that is very important, and I mentioned at the outset that among the variables is the degree of dispersion of dye. With the dyes that we use, Orange 2 and Methylene Blue, in the range in which we use them, I believe the particle size would not be measurable in that degree of dispersion. The slope of those curves is quite considerable. I think the fact is important, but I do not think that can account for all the differences that we measured. We measured the total quantity of dye adsorbed and not the intensity of color, and measured the quantity chemically by analysis, although I am quite sure that the degree of dispersion does change with pH, and that that is a factor.

As I say, it is not possible to consider all of these factors at once and all anyone can do is measure certain aspects or variables, attempting to keep the others constant.

Wool, the thing on which we made most of these measurements, is a very reactive chemical substance. I do not think that we all realize that so much, and I have only come to realize it recently as a result of the work that Dr. Harris and his associates are doing at the Bureau of Standards on the Fellowship from the A.A.T.C.C., as you know, and those of you who go to Chattanooga will hear the latest reports on that work. I happen to be a member of the committee in charge of that work and hear about it beforehand.

Wool is really a very reactive chemical substance and we must not overlook that fact. No doubt silk is also.

Wool, as we indicated, is both acidic and basic in character. In addition to bringing the dyestuff up to the point of combination, which is really all that my discussion and measurements indicate, the fastness of the dye depends upon the chemical relations. But it seems to me that you must have the charges right, and by that I mean opposite, so that they really make contact by adsorption. You have, then, the two substances, the fiber and the dye under ideal conditions for chemical reaction. All that we mean by chemical reaction is probably a jump of an electron from one to the other, bringing about a more or less permanent combination, limited, as Dr. Alexander pointed out to a certain number of weeks, like the permanent waves that are advertised and guaranteed.

Chairman Freedman: I should like to throw this meeting open for discussion from the floor, to hear from some of the members present. Are there any questions that any of you care to ask?

Dr. H. De Witt Smith: Many of the acetate dyes that we use are insoluble in water and are used in the form of dispersions. I wonder if you have done any work with your recent apparatus on the charges on those?

Dr. Neville: No, we haven't. I would very much like to, because the results I have shown are simply for acid and basic dyes, where the nature of the charge is quite obviously seen, but with the dyestuffs that are really insoluble and merely dispersed in water, I think we can't predict the charges offhand. They would have to be determined and I would like to determine how they vary.

I am quite confident that there is an electrical charge on those particles, although they may be perfectly neutral salts, because we have measured a number of materials in the cataphoresis cell and I have never had anything which did not show a charge. Apparently inert materials, I don't know what you would choose as the ultimate in inertness, but it seems to me that carbon black in contact with water would be about as inert as anything you can imagine and they are always electrically charged. The charge on carbon particles is quite pronounced.

Mr. Dogan: With regard to the acetate dyes, in your illustration of Prussian Blue, would the finer grinding of the acetate color penetrate, that is, give you a greater value for color? You give an illustration of what per cent of Prussian Blue and the white material, the Dolomite—one per cent gave you three distinct and different shades in concentration. Would that apply also to a colloidal acetate color, with regard to the dyeing of the acetate of celanese silk?

Dr. Neville: I would say that it would. You come to an optimum condition. I know, for example, work has been done with zinc oxide, relating particle size to opacity and covering power, and so on, and they find the curve is quite sharp. Suppose you take particles with decreasing radius and measure the opacity against that. You will get a maximum opacity, and then a drop-off, because if you get the particles too small, while their total covering power is greater, that is, you spread them farther, they get too small to really reflect the light completely. When they get finer, they no longer reflect, but only scatter, and you don't get the complete hiding of the material underneath.

Mr. Dogan: May I refer also to your illustration of the drop of stearic acid solution, which when dropped on the surface of water solidifies? You mention that there is an internal structural difference between the surface, that is, the top surface and a bottom surface. Is there a physical difference also that is distinguishable to the eye?

Dr. Neville: No, I don't think that you can see it. The whole thing appears crystalline, and this surface layer is perhaps only a molecule deep. Perhaps there is a little tendency toward orientation deeper than that, that is, the surface that is next to the water. You have really this surface orientation in the case of this stearic acid, which does crystallize as opposed by the crystal forces. The crystal forces tend to make the stearic acid molecules go into a definite space lattice which shows that the great attraction of water for those groups is able to overcome these forces. I have done the experiment, and I know the fact about the spreading of water is really true.

Dr. Alexander: The work was originally done by the Frenchman, Devaux. The experiment was quoted by Devaux.

Dr. Neville: Can you answer his question about the physical appearance of it?

Dr. Alexander: I do not think that you determine any physical consequence of that. There is only one point in connection with that that I have heard, that the attraction between the water and the oriented molecules in contact with the water is so great that some have expressed the view that a monomolecular film of water is actually held there even when you dry it. It is very difficult to get things utterly free from water.

In the baking powder illustration, it is customary, I think, to dry the starch down to less than one per cent of water. If you use ordinary dry starch, it contains around twelve or more per cent of water, and that would be enough to permit a reaction to occur between the bicarbonate and the acid ingredient, but in making the baking powder, they super-dry the starch.

Again reverting to what Dr. Neville said, I do not want to throw any rocks, but I simply used the question of rotten fish to illustrate the possibilities in moonshine. Moonshine has a powerful kick, but that is another kind of moonshine. (Laughter.)

However, generally, looking at this whole question broadly, we have two kinds of effects. One is to bring the dye particles up to and in contact with the fiber, and the other thing is to get them to "stay put," to make more or less of a permanent dye, and that permanence is regu-

lated by whatever the fiber is to be subjected to later—to soap baths, to washing, to rubbing, one thing and another, and you all know how various dyes and fibers differ. Some stand certain kinds of treatment better than others do.

There is one rather interesting thing in connection with this matter of surfaces. You have often noticed that when you are rowing a boat, for example, the water dripping from the oars will form little drops which skim the surface. This seems to be due to the fact that air is absorbed around the freshly formed surfaces of the drops, and air is absorbed on the surface of the water, so that if the drop and the water are of precisely the same chemical composition, it takes a certain time for that film of air to be displaced so that the drop of water can get down into the main mass of water. Somebody actually proposed that as a means of determining when two things are of identical or practically identical composition, by watching this "swimming drop" effect, you can match one solution up against another and determine when you got the maximum effect of this drop formation. Then you had precise balance between the two solutions, as proven later on by chemical analysis.

Mr. Dogan: I understand you to say that there was a certain dyestuff, dyeing pectin, and from this distance I understood you to say Ruthenium.

Dr. Alexander: Ruthenium Red, and I have not been able to get any of it, but it is mentioned in Dr. Farr's paper.

Mr. Dogan: Is that an aniline dyestuff?

Dr. Alexander: I don't know. I think I have the paper here, and I don't think it states precisely the source of this Ruthenium Red.

Dr. Smith: I have always thought it was an aniline dye.

Mr. Dogan: Perhaps it is some chloride.

Dr. Alexander: My impression is that it is a definite biological stain*.

Dr. Smith: I do not think it is a dye that is used at all in textile properties.

Mr. Emich: I would like to say for the information of the people here that this week's *Time Magazine* carries a very nice write-up concerning Dr. Farr and her theories, although I haven't seen it.

Mr. LaVene: I would like to ask a question with respect to what you mentioned about that powder, where it gets smaller than a certain amount of the dyestuff and does not have a proper covering capacity, and that when you get above a certain point, it also does not have the proper covering capacity. Did you in that study determine the proper size to get the best covering capacity?

Dr. Neville: I was quoting results given by the New Jersey Zinc Company, who are in the business of making zinc oxide of the maximum covering power.

*I have since found that it is ammoniated ruthenium oxychloride ($Ru_2(OH)_2Cl_4.7NH_3.3H_2O$), a stain used by microcopists as a reagent for pectin, gum and plant mucin.

The papers are "Industrial Engineering and Chemistry," about 1926. I can't tell you exactly, but it is about page 58, January number. (Laughter.)

Chairman Freedman: We have listened to a very interesting discussion this evening on surface chemistry. It would appear to me for one that the work being done by the research committees of the American Association of Textile Chemists and Colorists, and the work particularly of Dr. Neville and his associates, Dr. Harris, and others, should prove of inestimable benefit to the dyers and to the textile industry in general.

Seeing the many specimens of textile fabrics, as they are delivered to distributors for consumer use, and noting the great variations that exist in dyed fabrics purporting to come from the same thing, the need for extending research work, especially along the lines indicated this evening, seems to be quite evident and I think it is quite certain that we owe Dr. Neville a unanimous vote of thanks for coming down here this evening and opening up these new vistas of thought to us. I suggest that we all rise and give Dr. Neville a standing vote of thanks.

. . . The audience arose and applauded . . .

. . . The meeting adjourned at ten-thirty o'clock . . .

ONE HUNDRED AND SEVENTH COUNCIL MEETING

THE Council held its 107th meeting at the Penn Athletic Club in Philadelphia on Friday morning, April 10th at 10:30. Present were President William H. Cady, presiding; Elmer C. Bertolet, Vice President; William R. Moorhouse, Treasurer; Louis A. Olney, Chairman of the Research Committee; Elvin H. Killheffer and Robert E. Rose, Past Presidents; Carl Z. Draves, Henry F. Herrmann, Arthur E. Hirst, and Donald H. Powers, Councilors at Large; Eugene C. Knaeble, Hans Meyer, and Ben Verity, representing Philadelphia, New York and Rhode Island, respectively; and Harold C. Chapin, Secretary. The report of the 106th Council meeting was approved as published, and the Secretary's balance sheet of April 9th, attached hereto, was accepted.

To ratify existing practice, the ten dollar Sustaining membership fees and similarly classified contributions received in this fiscal year were formally voted into the Research Fund, and it was further voted that the solicitation of Sustaining membership fees hereafter be for the support of research. Following a discussion of Section expenditures and allowances from the treasury of the Association, it was voted that the Treasurer and Secretary prepare a summary of recent reports from Sections, for the guidance of Sections desiring to conform with general practice. There was discussion of possible amendments to the Constitution to give the Council discretion in requiring lower dues for admission or re-instatement after the middle of a fiscal year; also to permit more latitude in choice of month for the Annual Meeting in 1937 or thereafter.

SECRETARY'S BALANCE SHEET—APRIL 9, 1936

	Applications	*Dues, Regular and Re-instate*	*Dues, Sustain and Contributing*	*Dues, Corporate*	*Miscellaneous*	*Bank Charges*	*Totals, Net*
Received by Secretary, Nov. 1, 1935 to March 5. 1936	$570.00	$5,477.85	$240.00	$1,575.00	$482.19	—$2.33	$8,342.71
Received by Secretary, March 5, 1936 to April 9, 1936	157.50	1,157.50	15.00	100.00	56.27*	— .50	1,485.77
Total receipts	727.50	6,635.35	255.00	1,675.00	538.46	— 2.83	9,828.48
Transmitted to Treasurer	700.00	6,407.85	255.00	1,675.00	533.46	...	9,571.31
Leaving to order of Secretary	27.50	227.50	.....	.....	5.00	— 2.83	257.17

***Miscellaneous Items**

Knitted tubing	$8.27
Dyed standards	48.00
Total	$56.27

Conditional upon requested appropriations from the Textile Foundation and the Chemical Foundation, the program and salaries for Research Associates recommended by the Research Committee were approved. It was voted that the next Council meeting be in Boston at 10 A.M. on Friday, June 12th.

Each of the following was elected to the class of membership specified, as of thirty days from publication of application, provided that no objection be received meanwhile by the Secretary.

Active

J. S. Adamowicz
M. G. Ammann
Claude Bigat
A. H. Bock
L. P. Brick
Jesus Castro
F. E. Cater
J. J. Chateau
F. B. Clemmons
A. A. Cook
J. E. Crosland
C. G. Ewen
Maurice Goldemberg
D. T. Hatton
R. P. Hawkins
Rudy Herzfeld
J. D. Hunter
A. H. Kranstover
L. S. Lang
K. A. Lister
Oskar Loehr
W. F. McMahon
J. F. Monaghan
E. L. Moore
H. L. Nash
J. F. Newhouse
A. C. Orthmann
G. E. Osha
Wilbert Schod
James Shanks
F. M. Stevenson
D. E. Truax
J. K. Wilkie

Junior

P. M. Barnett
E. J. Brittan
L. H. Crosson
J. E. Greer
G. A. Poovey, Jr.

Associate

O. W. Bertram
W. O. Owens
J. Y. Pharr
J. H. Zahn

Student

K. V. Chace
C. B. Cooper
W. H. Pope
H. H. Williams

The following were transferred from other classifications to Active—H. B. Marshall, W. H. Moon, Arthur Spalding, W. B. Tucker.

Respectfully submitted,

H. C. CHAPIN,
Secretary.

ONE HUNDREDTH MEETING, RESEARCH COMMITTEE

THE 100th meeting of the Research Committee followed the morning meeting of the Council in Philadelphia, at 2 P.M. on Friday, April 10th. Present were Chairman Louis A. Olney presiding; E. C. Bertolet, J. R. Bonnar, W. H. Cady, C. Z. Draves, Alban Eavenson, H. F. Herrmann, A. E. Hirst, E. H. Killheffer, E. C. Knaeble, H. F. Lawton, Hans Meyer, W. R. Moorhouse, G. A. Moran, H. A. Neville, D. H. Powers, R. M. Ritter, R. E. Rose, Ben Verity, and H. C. Chapin.

The Chairman presented recommendations of the Committee on Research Program for continuation of the researches already in progress. These were accepted and referred to the Council. Mr. Cady reported on recent work of Dr. Glarum in collaboration with Dr. Strachan, on consistency of printing pastes. The Committee on Chemistry of Wool Fiber was represented by Mr. Eavenson, Chairman, Dr. Neville, Dr. Rose and Dr. Powers. Mr. Eavenson discussed recent work of Dr. Harris with Dr. Crowder and Mr. Smith. It was reported that Dr. Crowder had resigned to accept another position, but that the financial support of the Chemical Foundation would be continued. Dr. Olney reported on Mr. Ryberg's work under direction of the Committees on Determination of Fibers in Mixtures and on Determination of Extraneous Matter in Textiles; also for Mr. Edelstein, under direction of the Mercerizing Committee.

An invitation from the American Society for Testing Materials to appoint an Association member to its Soap Committee, was left to further consideration of the Chairman of the Research Committee. Standard procedure for the new crocking machine was discussed.

Respectfully submitted,

HAROLD C. CHAPIN,
Secretary.

MEETING, NEW YORK SECTION

THE last regular monthly meeting of the New York Section was held at the Alexander Hamilton Hotel in Paterson, N. J., on Friday, March 27th, at 8 P. M. Harry Price of the Celanese Corporation of America spoke on the "Dyeing of Celanese", describing in detail the boil-off, dyeing and finishing of Celanese piece goods, from the viewpoint of the practical dyer. Dr. H. D. W. Smith of A. M. Tenney Associates led the discussion. Dr. Paul Shlack of Acetate G M A H, Berlin, Germany, was present as a guest.

For the Annual Outing to be held in the latter part of June, probably at the North Jersey Country Club in Paterson, Henry F. Herrmann was appointed Chairman of a committee comprised of Daniel L. Clarenbach, Louis J. Dogin, R. Fitzgibbon, Robert Gaede, John D. Huizeng, P. J. Kennedy, J. L. Naylor, Arthur Wiehl, and Lloyd H. Winnell.

Attendance was 95. Chairman Ephraim Freedman expressed his appreciation of the attendance at all the meetings of the season.

Respectfully submitted,

P. J. KENNEDY, *Secretary.*

MEETING, NORTHERN NEW ENGLAND SECTION

A MEETING of the Northern New England Section was held on Friday, April 3 at the Hotel Manger in Boston. "Acetate Rayon" was the subject of the meeting and the following papers were presented: Dr. V. L. Bohnson, Manager of Chemical Research, Acetate Division of the duPont Rayon Co. spoke on "The Manufacture and Properties of Acetate Yarn." Mr. Philip Stott of the Technical Laboratory of the duPont Dyestuffs Division gave an account of recent developments in the dyeing of acetate rayon. The section is indebted to both speakers for their very fine description of the different phases of acetate rayon production and a very interesting and profitable evening was spent by the nearly 100 members present.

Respectfully submitted,

JOHN N. DALTON, *Secretary.*

MEETING, PHILADELPHIA SECTION

THE fifth meeting of the 1935-1936 season was held on Friday evening, April 10th, 1936, at the Broadwood Hotel in Philadelphia.

The Chairman of the Program Committee, Mr. William A. Stringfellow presided at the dinner and business meeting, and introduced our guests of the Council and Research Committee, many of whom were present, following their meetings held during the day at the Penn Athletic Club.

President Emeritus, Louis A. Olney, and President William H. Cady responded with brief messages. Mr. Cady directed attention to the question of changing the annual convention date to the spring or autumn season, starting with the year 1937.

In the absence of the Secretary, the reading of the minutes of the previous meeting was suspended.

Mr. Henry E. Millson, Chairman, presented a brief review of the objects and activities of the Open Forum, and read the questions presented for consideration since the last meeting. These will be made part of the next meeting notice.

Mr. Elmer C. Bertolet, Vice President and Chairman Emeritus of the Section, then introduced the guest speakers of the evening.

Dr. Harold DeWitt Smith, Treasurer and Textile Technologist of the A. M. Tenney Associates, Inc., sales representatives for the Tennessee Eastman Corporation, presented a very interesting and instructive paper on "The Manufacture and Properties of Eastman Acetate Yarn", which he illustrated with numerous slides.

Dr. Ivor Griffith, Director of Research, John B. Stetson, Philadelphia, followed with an address on the "The Dyeing of Fur Felt".

Brief discussions followed both talks.

The meeting adjourned following a rising expression of thanks to the speakers.

The attendance approximated ninety.

Respectfully submitted by

CHARLES A. SEIBERT,

Acting for the Secretary, Robert W. Delaney.

CALENDAR OF COMING EVENTS

Meeting, New York Section, Chemists' Club, New York City, May 22, 1936. Speaker: Dr. Feibelmann, Aktivin Corp., Inventor of "Aktivin"; Subject "Hydrosulfite and Vat".

* * *

Outing, Philadelphia Section, May 22, 1936, Manor Country Club, near Reading.

* * *

Council Meeting, Boston, Massachusetts, June 12, 1936, 10 A. M.; Research Committee meets at 2 P. M.

* * *

Outing, Rhode Island Section, June 18, 1936.

* * *

Summer Meeting and Outing, Piedmont Section, June 27, 1936, Ocean Forest Hotel, Myrtle Beach, S. C.; reservations through Mason Alexander, manager.

* * *

Annual Meeting, Providence, R. I., December 4 and 5, 1936.

AMERICAN
DYESTUFF
REPORTER

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Directing Editor

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Activities of the Textile Foundation

ADDITIONAL avenues of textile research of an economic character are to be explored as a result of recent appropriations made available by the Textile Foundation. It will be recalled that the Foundation was organized for scientific and economic research for the benefit and development of the textile industry, its allied branches, and including that of production of raw materials; and that Franklin W. Hobbs of Boston is chairman, Stuart W. Cramer of Cramerton, North Carolina is treasurer, and Frank D. Cheney of New York and the Secretary of Agriculture and the Secretary of Commerce constitute the Board of Directors.

Four research fellows whose terms expire during the spring or summer were reappointed for a period of one year to continue research work on textile fibers. The Foundation recently issued a list describing about fifty progress reports of its group of research fellows. A copy of this descriptive list may be obtained upon application to the Foundation in Washington.

Funds were allocated for the continuation and extension of the following projects: Fundamental Study of Vat Printing Pastes, The Effects of Oxidizing and Reducing Agents on Wool, and a further study of The Chemistry of Wool Fibers, The Quantitative Determination of Fibers in Mixtures, and, The Determination of Oil, Soap and Other Extraneous Material in Wool and Various Stages of Wool Processing. This work is to be continued under the supervision of the American Association of Textile Chemists and Colorists.

Some months ago a survey of textile waste treatment and recovery was initiated and a compilation of fundamental and widely applicable information is now being prepared for publication. During the course of this survey, it became apparent that little fundamental research on this important problem has been undertaken and upon recommendation of those who conducted the survey and an advisory committee of a number of the country's leading authorities on waste disposal, the Foundation is about to undertake fundamental research on The Colloidal and Electric Nature of the Polluting Substances Carried in Textile Wastes, and investigate means for removing these substances from the wastes.

In addition to this type of research, small plant scale work will be carried out to develop the practical applications of the laboratory findings and conduct research on the problem of refining municipal sewerage which contains considerable amounts of textile wastes.

As a corollary to these two specific research jobs, there will be established a clearing house for the collection and distribution of information on work other than that directly authorized by the Foundation. It is expected that this clearing house will in time be able to furnish information to textile manufacturers, engineers and others dealing with textile waste problems, but of course the clearing house will not assume the capacity of a professional consultant.

A grant was made for financing a study on "Production and Distribution Organization in the Textile Industry." This study will be conducted under the advisory supervision of the Committee on Economic Research of the U. S. Institute for Textile Research which recommended the subject to the Foundation. The Committee will appoint a research agency for the active conduct of the work.

This announcement is of particular interest in that the Foundation in the past has financed several investigations into distribution policies and methods in specific branches of the textile industry, and is now sponsoring an over-all survey of importance to the industry as a whole. The project has the endorsement and cooperation of the presidents of four of the major textile associations who will also act in an advisory capacity during the conduct of the study.

This trend study will involve, particularly, investigation into the factors affecting the success or failure of various types of organizations which have undertaken at any important point, to bridge the gap between mill and consumer. It will be based, not upon theoretical considerations, but upon the actual experience of a number of companies—both within and without the textile industry.

There are many important examples of such developments: Mills which manufacture garments, garment manufacturers who have bought mills or who control retail stores, wholesalers who convert their own goods, mills or converters who have worked out close cooperative arrangements with wholesale or retail distributors, etc., etc. It is realized that no categorical conclusion can be reached in such a study; its main purpose is to indicate under what conditions such arrangements seem to have been successful—and, similarly, what conditions seem to have contributed to their failure. These facts, it is felt, will be of great help to individual manufacturers as guidance in their own determination of future policies.

Cotton-Warp Sizing

(Continued from page 260)

yards of sheeting, followed successively by a cushion of 4 yards of composition cloth (70 per cent cotton), 2½ yards of a 70 per cent wool blanket, and finally with slasher cloth.

In changing blankets on the first or front roll, it is recommended that the older blanket be put on top, if two pieces of cloth are used; if only one piece is used, the blanket from the second roll is transferred to the first roll. It is claimed that the older and better-seasoned blanket cuts off the size better and prevents slipping of the yarn between the squeeze roll and the size roll. A fresh blanket on top tends to leave more size in the yarn. In changing slasher cloth on the second roll, it is suggested that it first be used on the front roll for several days. This will stretch the blanket and prevent the size-roll from slipping.

It is stated that slasher cloths should be removed for washing at intervals of three to four weeks, sometimes oftener. The washing should be carried out in boiling water, care being used that no steam comes in contact with the cloth. Some soak the blankets over the week-end to keep them pliable and others wet-out about a yard of the blanket for a period of an hour upon starting after the week-end.

Mill men are advised in replacing one roll to replace both, because the rolls are so constructed that after running for a number of years there will be a sag between the ends and the center brace. If the diameters of the size rolls are not exactly the same, the yarn will be stretched.

SPEED OF SLASHERS

Slasher-speed depends on the number of the yarn, the number of ends, the temperature of the drying cylinders, and the percentage of size and moisture in the sized yarn. In general, the lower the number of ends, the faster may the slasher be run. It is claimed that with complete temperature controls—i.e., on cooking and storage kettles, size-box, and cylinders—more uniform size take-up and moisture content, and greater speed at the slasher are possible. Much greater speed is also obtained on slashers provided with a new stretch-control mechanism, as explained later. Table I (gathered from reports of discussions at meetings of mill-men and other sources) arranged according to the number of ends, shows the speed of the slasher, numbers of the yarns, temperatures of the cylinders, percentages of size and moisture on the yarn, and whether or not temperature controls were used.

STICKING OF YARN TO CYLINDERS

Causes.—The sticking of yarn to the cylinders on slashers may be caused by anyone of several conditions and is experienced more generally by mills using thick-boiling starch or a very heavy or concentrated thin-boiling

Fig. 3—The Saco-Lowell New Slashing System

1.—Head-end Yardage Clock.
2.—Yardage Clock operated from Stretch Control Unit.
3.—Roller Bearings on Delivery Roll, Top Back Press Roll and Measuring Roll. Roll Lifting Mechanism.
4.—Whitman Lever Friction.
5.—Self-Aligning Oil Ring Bearings on Front and Back Cone Shafts.
6.—Measuring Roll—operating Cut Marker.
7.—Self-Releasing Device, driving 7-foot Cylinder.
8.—Self-Releasing Device, driving 5-foot Cylinder.
9.—Sight Glass on Condensate Lines.
10.—Tycos Cylinder Temperature Control and Recorder.
11.—Weighting and Lifting Mechanism for Squeeze Rolls in 2-Roll Vat.
12.—Size Supply Pipes.
13.—Level Control Valve for size in vat. Temperature Control Instruments are on opposite side.
14.—Stretch Control Device.
15.—Change Gears for Stretch Control.
16.—Drawing-In Frame for counting-in the warp.
17.—Comb for Drawing-In Frame.
18.—Section of Double Creel.
19.—Creel Trucks.
20.—Creel Tracks.
21.—Roller Bearings on Beams in Creel.
22.—Roll to support Yarn and Comb while moving Creel into position in rear of Slasher.
23.—Other Section of Double Creel.
24.—Stretch Control Device and Size Vat, showing Automatic Temperature Control Instruments.

Courtesy, Saco-Lowell Shops

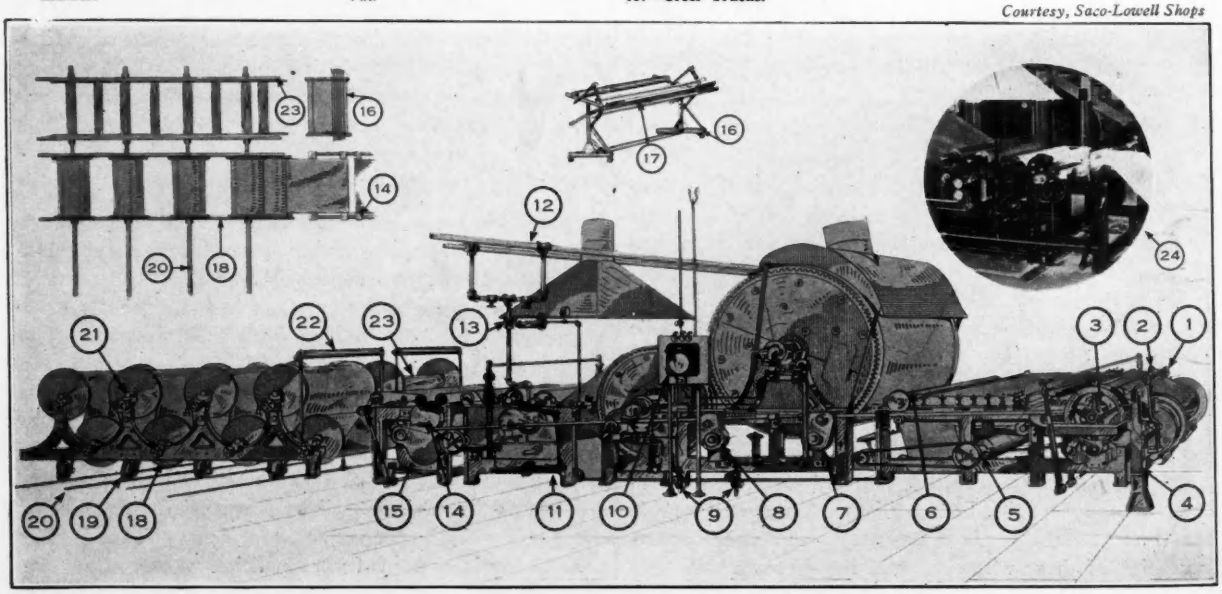


TABLE I

No. of Ends	*Speed of Slashers, Yds./Min.*	*No. of Yarn*	*Tem.of Cylinders, ° F Large*	*Small*	*Moisture %*	*Size %*	*Temperature Controls*
483	65	30s	...	...	...	....	Everything but cylinders
1600	40	26s	...	...	...	....	.....
1980	60	30s	...	...	...	....	Everything but cylinders
2170	65	55s	232	240	6	10	Complete control
2480	33	30s	232	240	8.5	13.5	Complete control
2500	35	25s	...	...	...	....	Everything but cylinders
2626	30	24s	...	...	...	....	Everything but cylinders
3000	35	22s	...	...	...	....	.....
3120	45	30s	230	240	8 to 8.5	8	.....
3146	32	30s	...	...	7.7	11.5	No controls
3186	35	30s	...	...	...	....	Everything but cylinders
3200	35	30s	...	...	...	....	Everything but cylinders
3700	30	30s	...	...	...	....	No controls
3900	28	24½s	224	234	...	....	Complete controls
4100	47	30s	230	240	8to 8.5	10 to 11	.....
5740	17	21s	242	252	6	8	Complete controls

starch mixture. Sticking may be caused by the poor condition of the blankets on the squeeze rolls, or the squeeze rolls may not be heavy enough to squeeze out the excess size, especially if the set being run is a heavy one. Sticking may also occur if there is an insufficient amount of softener used. Other causes may be (a) insufficient cooking of the size, (b) too low a temperature (under 200° F.) in the size box, (c) immature cotton, (d) bumps on the face of the cylinders, and (e) dirty or gummy cylinders.

It was also found that condensation in the cylinders may be the cause of the sticking. When condensation occurs the cylinders are not hot enough to dry the yarn properly, leaving wet starch on the cylinders. The wet starch ultimately dries and may be the cause of binding the warp to the cylinder.

Remedies.—To overcome sticking to the cylinders, it has been suggested to make sure that the squeeze rolls are heavy enough and the blankets in good condition. It is also recommended that at least 8 pounds of tallow-fat be used per 100 pounds of starch. It will also be advisable to see that the slasher-cylinder is thoroughly cleaned by brushing with soap and water. A pint of turpentine or kerosene stirred in with the size-mix after the cooking is completed and before the size is turned into the size box, will usually clean off cylinders and stop the sticking. The temperature of the cylinders should be regulated to take care of the complete drying of the warps. The first cylinder should preferably have less heat than the following one. This is to avoid baking, blistering, or burning of the yarn which may take place when it comes in contact with an overheated surface. Gradual drying is most essential and will give the best results.

DRYING OF WARPS

Drying at a high temperature lowers the hygroscopic capacities of both cotton and starch. It is stated that drying at the temperature of boiling water decreases the strength of unsized yarn about 2 per cent. It is presumed, although not fully established by test at the time of writing, that over-drying will aggravate the brittleness of sized yarns. It is a well-known fact that the size-film of a warp dried to a state where there is a deficiency of moisture, has lost the greater part of its elasticity, with the result that in weaving not only will its weakness cause excessive breakage, but there will be a good deal of shedding. Excessive baking will usually cause scales like small dandruff to drop on the floor of the weave room, as well as considerable shedding of small fibers. A practice that causes trouble is the occasional stoppage of the slasher, for one reason or another, with the result that 20 to 40 yards of warp become dried to an extent where the weaving properties of the yarn are greatly damaged.

MOISTURE-REGAIN

Effect on Tensile Strength.—High humidity causes swelling and consequent better gripping of the cotton fibers, hence stronger yarn. The greatest strength of sized yarn, however, is reached at about 70 or 80 per cent relative humidity. Above that, it falls off on account of loss of strength of the softened starch. Size causes better gripping by its cementing action and makes the yarn stronger under ordinary conditions. As the size softens at high humidities its effect is lost and yarn has the same strength at saturation whether sized or unsized. Sizing decreases the extensibility under dry conditions but it is rapidly regained with increasing humidity. At saturation it approximately equals that of the unsized yarn. Since sized cotton yarns are more extensible at higher humidities than at lower humidities, weaving sheds in which heavily sized goods are made are usually kept very humid.

Rate of Regain.—Ordinary cotton yarns are stated to come to equilibrium following a change of atmosphere in about 30 minutes, most of the effect taking place in the

first few minutes. The presence of size decreases this rate of change by about a third. Tire cord requires about 15 hours to come to equilibrium in a moist atmosphere; cotton fabrics of average weight, about 3 hours. Loose fibers with an almost perfect exposure to the air will change their regains very quickly. Raw stock in bulk will take a longer time to condition through and through, because a great deal of the air at the new relative humidity must penetrate and diffuse through the mass before the necessary amount of water can be brought to the cotton or carried away from it. Obviously, for conditioning textile materials it is best to have the air in motion; but whether moving or not, if it is of constant humidity, the material will come to equilibrium and stay there.

Absorption of moisture by cotton proceeds very quickly according to the water-vapor pressure, because fiber-colloids tend to take up particles of water very avidly. On the other hand, they give up water more slowly, for even at a low vapor pressure in the room as compared with the tension of the water retained by the fiber, the latter has the tendency (owing to its colloidal nature) to retain the particles of water as firmly as possible.

Moisture Regain of Cotton Yarns and Cloths.—A careful survey among a number of mills has shown that the average moisture regain of finished yarn in mills where humidifiers were running was 6.95 per cent and in mills where humidifiers were not in operation in the finishing department, 4.44 per cent. The average regain of finished cloth in mills where humidifiers were running the cloth-room was 7.58 per cent and where humidifiers were not running, 5.67 per cent. The average regain in the finished cloth ready for shipment was 6.6 per cent. The moisture regain of cotton at different relative humidities is reported to be as follows:

Realtive Humidity	*Moisture Regain*
%	%
60	7.5
70	8.8
95	18.0
100	33.0

Standard Atmosphere.—The standard atmosphere for conditioning cotton for tests is a relative humidity of 65 per cent, with a tolerance of plus or minus 1 per cent, and a temperature of 70° F, with a tolerance of plus 10° F. Tests on cotton have shown that a rise in temperature of 10° F. has approximately the same effect as a drop of 1 per cent in relative humidity.

Moisture in Warps.—One mill recommends for good weaving on coarse warps under 20s, a moisture content of 7 per cent to 8 per cent. Other moisture figures mentioned are 6½ per cent to 7½ per cent on 30s yarn, 1980 ends; and 6 per cent to 7 per cent on 8-ounce ticking.

SHEDDING

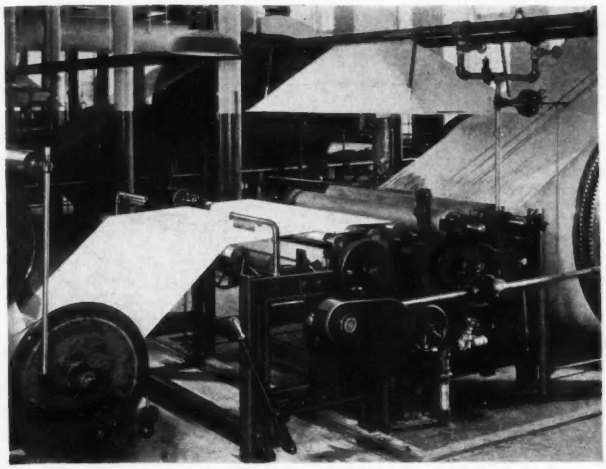
There may be other local conditions that cause shedding, but in general it is due to improperly or insufficiently cooked starch, too viscous or heavy size, too low a temperature in the size-box, or excess of fatty matter in the size. If shedding is being experienced and the starch is being thoroughly boiled, it is advisable to determine whether or not the size is sufficiently thin to permit proper penetration of the yarn. If not, a thinner starch should be used. Proper penetration of the yarn is sometimes prevented by too low a temperature of the size in the size-box, causing thickening or increased viscosity of the starch. This condition can, of course, be rectified by arranging for better heating and for sizing at a higher temperature. Excess tallow often causes shedding as it has a tendency to reduce the adhesiveness of the starch to the warp.

STRETCH OF YARN

In the case of cotton, surprising results have been achieved by uniformly controlled stretch at approximately 1 per cent. The natural gray yarn has a stretch of only 6 per cent to 7 per cent at the breaking load and some cotton slashers in operation today actually take out as much as 3 per cent stretch, or approximately one-half. This is sufficient to seriously weaken the yarn, particularly where the maximum stretching occurs at places that are already thin as the yarn enters the slasher. In many cases, slasher speeds have been limited by the factor of excessive or irregular stretching. Warps were made with zero stretch, but under this condition the yarn comes off the slasher slack and it is impossible to attain high speeds due to the poor splitting at the lease bars. However, it was found that there is practically no difference in loom efficiencies between warps having zero stretch and 1 per cent, but beyond 1 per cent the efficiencies drop very quickly.

One mill reports that yardage-counters installed on the front and back of the slasher provide a simple means of determining the amount stretch in the yarn during slashing. It was found by one mill that approximately 1 per cent stretch occurred between the squeeze roll and the pulling roll on the front of the slasher. Another mill had installed yardage-counters driven by surface contact on the beams, both front and back, and found a total stretch of 1.85 per cent to 2 per cent; this method showed more stretch than when measured from the delivery roll. In a discussion on stretch of yarns during slashing, one mill reported practically no tension on the slashers. Other mills reported as follows: on 30s yarn, 0.94 per cent to 1.5 per cent; on 12s to 17s yarn, 1.25 per cent; on 26s yarn, 1692 ends, 0.1 per cent to 0.6 per cent; and on 12s yarn, 0.4 per cent to 1.3 per cent.

Stretch-Control Device.—There has recently been put on the market a device for controlling the stretch of yarn on the slasher. It is claimed that with this device the speed of delivery may be more than doubled, with even better slashing and weaving efficiencies than at the slower speeds with no controls. The speed of the slasher with this system seems to be limited by the drying capacity of the cylinders. It is also claimed for the stretch-control device that besides greater production, it produces warp and loom beams of unusual uniformity with respect to



Courtesy Saco-Lowell Shops.

Fig. 4—Showing Application of Stretch Control Device Between Creel and Size Box

strength and elasticity, due to the even application of the size and to holding the stretch of the yarn at a uniform and predetermined minimum. To obtain the full benefit of the increase production made possible by the stretch-control device, a special double creel is used, by means of which it is feasible to have unskilled labor count and lease a new set in advance of the time it is required in the slasher.

In the old type slashers it is stated that irregularities in stretch are due, first, to the yarn slipping on the size rolls as it is drawn from the creel and, second, to the effect of varing weights and tensions on the section-beams. Moreover, the yarn is subjected to excessive strain just after leaving the size-box, when it is wet and therefore most easily stretched.

Instead of the yarn being drawn from the creel, the new device provides a positive feed to the size-roll, delivering the yarn to the size-box at a definite speed. As shown in Figure 4, this is accomplished by taking the yarn off the creel over a 9 inch flannel-covered roll, the yarn being held in contact around 80 per cent of the roll-circumference by means of two small idler rolls. The stretch is controlled by adjusting the relative speeds of the feed rolls and the head-end delivery rolls. The head-end delivery roll is geared to the size-box as a unit, so that any desired amount of stretch from zero to the maximum amount of elongation of the yarn is readily obtained by the change gear selection, which determines the relation between delivery-roll speed and feed-roll speed. The gear train is so designed that 100-tooth change gear gives a zero stretch; a 101-tooth gear, 1 per cent stretch; a 102-tooth gear, 2 per cent stretch, etc.

CARE OF SLASHER-CYLINDERS

Dents in Cylinders.—The condition of the cylinders plays an important part in getting an evenly dried warp. Dents, which are common in most slasher cylinders, are outward knobs protruding above the otherwise smooth copper surface. These dents not only affect the drying efficiency of the cylinder, but also the life of the copper itself. Warps passing over the cylinder contact these high places and in doing so are lifted above the cylinder elsewhere. Wherever this occurs, the warp does not make contact with the hot copper as does the remainder of the warp, thus causing uneven drying. The increased friction occurring constantly on these dents adds considerably to their wear and, if allowed to continue, will eventually wear through the copper.

Loose solder from the buckets and parts of the buckets themselves falling around in the cylinder cause these dents. Bad buckets are usually responsible for the copper on cylinders becoming bulged and, in most instances, the cause of the cylinder-heads blowing out. This is due to the buckets not removing the condensed water and thus letting the water-load get above the tensile strength of the copper. Water in contact with the bottom of the cylinder also lessens the efficiency of the cylinder by lowering the temperature there.

Patching Holes.—A great many holes and leaks in cylinders have been patched by soldering. Others have copper patches riveted over them and solder over the rivets, while some are brazed with bronze. All of the above will stop the leak temporarily, but leave a great hazard, for in addition to the repair being temporary considerable thickness to the copper is added. This reduces the efficiency and creates a rough place which may snag the warp threads.

A great many cylinders begin leaking at the seam. These fractures occur more often on the large cylinder than on the small one. This is due to the fact that there are two seams in the large cylinder and only one in the small cylinder; also because the large cylinder is subjected to greater stresses. When these fractures occur, the sooner they are repaired the better, otherwise they will continue to tear until they have reached the outside heads. When a fracture-seam extends to the head, it is necessary to remove the cylinder from the frame and take the heads off to make repairs.

LOOM STOPS

An analysis of the production from the looms made by the British Cotton Industry Research, showed that the rate of breakage of warp threads was controlled by the sizing, and therefore the weaving was also dependent on the amount of size on the warp. When the broken threads were examined for the cause of break, it was often possible to find an imperfection in the yarn which caused the breakage. The place of breakage was considered and the breaks occurring between the beam and heddles were few and independent of the amount of size. In the heddles the breakages were fairly frequent in undersized warps, falling off where sufficient size was present, and tended to increase again when the amount of size was excessive. In the reed the number of breakages was fairly steady except in undersized warps.

The number of loom stops per hour on various standard

constructions was found to range from 0.26 to 0.86 stops per loom. On constructions with average yarn numbers around 30s, 64 x 60, it was found that 0.75 to 0.85 stops per loom per hour is about normal. On coarser sheetings, however, the maximum was said to be about 0.75 stops per hour.

In mills where looms were equipped with feelers, equally as many or more loom stops were said to be caused by filling breaks as by warp breaks; but in weave rooms where feelers were not used, warp-yarn breakage was found to be responsible for a higher proportion of all loom stops. In one instance where feelers were not used, 70 per cent of all loom stops were said to be due to warp-yarn breaks.

ACKNOWLEDGMENT

The writer is very much indebted to M. D. Shaffner of the Saco-Lowell Shops and T. C. Hazard of the Taylor Instrument Companies for many valuable suggestions.

CLASSIFIED

POSITION WANTED—Experienced chemist and dyer on acetate rayon and silk is now available. Formerly connected with two of the largest organizations in the dyestuff and dyeing industry. Can furnish excellent references. Forty years of age, married, and willing to go anywhere. Box No. 880, American Dyestuff Reporter.

POSITION WANTED: By salesman who covered Philadelphia territory on oils, finishes, soaps, tints and dyes. Available at once. Write Box No. 903, American Dyestuff Reporter.

New Products—Trade Notes

● BROSCO PRODUCTS

"Brosco Products for Textiles" is the title of a recent booklet issued by Scholler Brothers, Inc. Manufacturing processes and laboratory control are described by reading matter and half-tone illustrations. The complete line of Scholler products for the textile field are listed. Copies are available upon request.

● SANDOZ RELEASE

Sandoz Chemical Works, Inc. announces release of a circular describing the following new product. Copies are available upon request.

Visco Blue R S—a level dyeing blue of unusual brightness. It is claimed that the fastness to washing, perspiration, alkalies, acids and hot wet pressing are outstanding features of this product when dyed direct. It is recommended by the manufacturers for the direct dyeing of rayon and cotton piece goods. It is also said to be useful as a combination color for novelty yarns composed of rayon and wool due to the level results on the rayon and the slight tinting on the wool. It is claimed that speck dyeing can be carried out very successfully because of its good affinity for cotton at low temperature. Light fastness is fair in direct dyeings but can be considerably improved by aftertreating with copper sulfate. In respect to its fastness properties and its exceptional brightness of shade it is said to be superior to the Pyrazol Fast Colors. Circular L.L. 66.

● CORRECTION
Re Printing Colorists

In the May 4th issue it was erroneously stated that a meeting of the New York-New Jersey-Pennsylvania Section of the National Association of Textile Printing Colorists would be held at the Elks Club in Paterson, N. J., on May 16th. This meeting was held by the Textile Printing Colorists Guild, Inc., which is not associated with the National Association of Textile Printing Colorists in any way.

● MAY ISSUE, TEXTILE RESEARCH

Progress and future plans of the warp sizing research that is being conducted by U. S. Institute for Textile Research, are reported in the May number of Textile Research by Wright Bolton, chairman of the committee in charge of this project. Other textile researches reported in this issue, in addition to the regular abstract section covering new research throughout the world are the following:

Conclusion of the Textile Foundation report on "Experimental Studies in Flax Growing, Decorticating, Degumming and Manufacture into Yarns and Papers;" "Creep in Single Fibers of American Delta Cotton," by R. L. Steinberger, a Textile Foundation Fellow; "An Optical Method for the Length Analysis of Cotton Fibers," by K. L. Hertel and M. G. Zervigon.

The Steinberger report continues the fundamental study of constant stress elongation, or creep, of textile fibers and filaments. This interesting phenomenon and its laws are basic to a number of textile processes, notably crepeing. Mr. Steinberger is accumulating data on the theory of crepeing.

The instrument and method for obtaining length-cumulative frequency curves of cotton fibers, described by Hertel and Zervigon, eliminates the necessity by other methods of fractionating the sample into length groups and the weighing or counting of the fibers to obtain the desired curves. However, the authors admit that a more representative and adequate sample should be used with their instrument, and they will report later upon such an improvement of method.

● GENERAL RELEASES

General Dyestuff Corp. announces releases of circulars on the following new products. Copies are available upon request.

Supramine Red G L—a new acid red brought out by the I.G. and offered to the trade by General Dyestuff. Dyed from a Glauber's salt—sulfuric acid bath it produces yellowish reds said to be of very good fastness to light, and also to have the additional advantage of fairly good fastness to washing and perspiration. It is further said to have good leveling properties and is recommended by the manufacturers for combination shades together with Supramine Yellow 3 G L and Alizarine Direct Blue A G G or A R A. It is stated that cotton, rayon and acetate effects are left perfectly white. It is further claimed that Supramine Red G L will penetrate well and should be of interest for hat dyeing; the very good solubility making it very suitable for machine dyeing and printing. It discharges to a clear white with Rongalite. Circular I. G. 1165.

Supramine Pure Blue B L—another new acid color brought out by the I.G. and offered to the trade by General. It is said to level well from a Glauber's salt—acetic acid bath and produces bright blue shades which, it is stated, have so far been unobtainable in such a combined good fastness to light, washing, perspiration and salt water. These fastness properties, it is claimed, make the new brand especially desirable for the knitting trade as a self color. The very good solubility claimed for it makes it very suitable for machine dyeing as well as for printing. It is further said that it has good affinity for pure and tin-weighted silk. Circular I.G. 1130.